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METALLOGRAPHY

THE METALS AND COMMON ALLOYS

METALLOGRAPHY

BY

SAMUEL L. HOYT

PART I.—PRINCIPLES

II.—THE METALS AND COMMON ALLOYS

III.—TECHNICAL PRACTICE

IN PREPARATION

METALLOGRAPHY

PART II THE METALS AND COMMON ALLOYS

BY
SAMUEL L. HOYT, E. M., PH. D.,

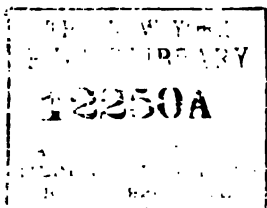
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PREFACE

The present book describes the more important metals and alloys. This description includes the constitution and micro-structure, the physical and mechanical properties for different conditions of heat and mechanical treatment, the effects of impurities commonly present and a brief discussion of the uses. Those compositions which have proven to be of particular importance have been treated more in detail, and in these cases I have given measured values of the important properties. These diagrams and tables have been selected with care so that they may be relied upon to give the normal behavior of the material in question. Other features which are included for their value for reference and study are critical point diagrams, constitution diagrams, structural diagrams and photomicrographs.

I am equally indebted here to those already mentioned in **PRINCIPLES OF METALLOGRAPHY**, for their assistance in the preparation of this volume. In addition I wish also to express my warmest thanks to Dr. Zay Jeffries for reading Chapter III on the Aluminum Alloys and permission to use photomicrographs and other material in the text, and to the Midvale Steel Company for permission to use information on certain of the special steels obtained in their Bureau of Research. I wish also to acknowledge my indebtedness to Dr. H. Hanemann for many of the photomicrographs used which were selected from his excellent collection.

S. L. H.

NELA PARK, CLEVELAND, OHIO.
January, 1921.

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METALLOGRAPHY

PART II

THE METALS AND COMMON ALLOYS

CHAPTER I

THE PURE METALS

Of the elements which may be considered to be the common elements, thirty-seven are metals or metalloids, seven are non-metallic, but alloy-forming elements, and only four (the halogens), do not enter into the metallic alloys. The common alloy-forming elements are here given in the abbreviated periodic

ABBREVIATED PERIODIC SYSTEM

II 1			B 11	C 12											N 14	O 16
	Na 23	Mg 24	Al 27	Si 28											P 31	S 32
	K 39	Ca 40		Ti 48	V 51	Cr 52	Mn 55	Fe 56	Ni 59	Co 59	Cu 64	Zn 65		As 75		
		Sr 88				Mo 96			Rh 103	Pd 106	Ag 108	Cd 112		Sn 119	Sb 120	Te 127
		Ba 137		Ce 140												
						Ta 182	W 184		Os 191	Ir 193	Pt 195	Au 197	Hg 201	Tl 204	Pb 207	Bi 208
						U 238										

FIG. 1.—The Common Metals and Alloy-forming Elements.

system in Fig. 1 in which the elements are arranged according to their atomic weights. The properties of these metals are given in Table 1, of which only the ones of more importance will be considered in detail.

TABLE 1.—PROPERTIES OF THE COMMON METALS

Metal	Symbol	Melting point, °C.	Boiling point, °C.	Atomic weight, 1920	Specific gravity	Specific heat, °C.	Linear coefficient of expansion at 40°C. $\times 10^6$	Electrical conductivity		Temperature coefficient, α	Thermal cond., °C.	Hardness No.	Color
								(a)	Cu = 100				
Aluminum	Al	658.7	1800	27.1	2.56	0.2089	0.2313	38.2	61.5	0.0039	0.3435	2.9	Tin-white
Antimony	Sb	630.0	1440	120.2	6.70	0.0495	0.1152	2.565	0.0442	3.0	Silver-white
Arsenic	As	850 ?	360	74.96	5.73	0.0758	0.0559	2.85	3.5	Steel-grey
Barium	Ba	850	950	137.37	3.5	0.0680	Yellowish-white
Bismuth	Bi	271	1430	208.0	9.76	0.0301	0.1346	0.929	...	0.0046	0.0177	3.5	White
Cadmium	Cd	320.9	778	112.4	8.7	0.0548	0.3069	14.41	...	0.0042	0.2200	2.0	White, blue tinge
Calcium	Ca	810	...	40.1	1.82	0.1453	...	13.3(6)	1.5	Yellowish-white
Cerium	Ce	640	...	140.25	5.5	0.04479	...	1.395	Steel-grey
Chromium	Cr	1615	2200	52.0	7.0	0.10394	...	38.5	9.0	Greyish-white
Cobalt	Co	1480	...	58.97	8.74	0.1030	0.1236	8.32(c)	...	0.0037	...	5.5	Steel-grey
Copper	Cu	1083.0	2310	63.57	8.65	0.0939	0.1678	63.4	100	0.0041	0.7198	3.0	Reddish
Gold	Au	1063.0	2530	197.2	19.3	0.0316	0.1443	44.5	70.2	0.0037	0.7003	2.5	Yellow
Iridium	Ir	2350 ?	...	193.1	22.4	0.0323	0.0700	16.4	...	0.0039	...	6.5	Grey
Iron	Fe	1530	2450	55.84	7.86	0.1338	0.1182	9.36	14.8	0.0062	0.1587	4.5	Greyish-white
Lead	Pb	327.4	1525	207.2	11.4	0.0315	0.2924	5.05	...	0.0043	0.0836	1.5	Blue-grey
Lithium	Li	186	1400	6.94	0.58	0.78-0.795	...	11.7	0.6	Silver-white
Magnesium	Mg	651	1120	24.3	1.75	0.2456	0.2694	23.2	36.6	0.0038	0.3760	2.0	White
Manganese	Mn	1230	1900	54.9	8.0	0.1072	...	18.2-22.7	5.0	White
Mercury	Hg	-38.9	357	200.6	13.6	0.0334	1.8200	1.063	...	0.0069	0.0148	...	Dull silver
Molybdenum	Mo	2550 ?	...	96.0	8.62	0.0650	0.0501	17.54	28.0	0.0033	0.316	...	White
Nickel	Ni	1452	...	58.68	8.5	0.1034	0.1279	14.42	22.7	0.0062	0.1420	3.5	White
Osmium	Os	2700 ?	...	190.9	22.48	0.0311	0.0680	10.53	...	0.0042	...	7.0	Bluish-white
Palladium	Pd	1550	...	106.7	11.4	0.0592	0.1176	9.39	...	0.0035	0.1683	4.8	White
Platinum	Pt	1755	...	195.2	2.15	0.0323	0.0899	8.49	13.4	0.0037	0.1664	4.3	White
Potassium	K	62.3	712	39.1	0.87	0.1876	0.8300	15.05	0.5	Silver-white
Rhodium	Rh	1950	...	102.9	12.1	0.05803	0.0850	21.3	...	0.0043	Bluish-white
Silicon	Si	1420	3500	28.3	2.0	0.2140	0.0763	7.0	White
Silver	Ag	960.5	1955	107.88	10.55	0.0556	0.1921	66.4	104.7	0.0040	1.0960	2.7	Silver-white
Sodium	Na	97.5	750	23.0	0.97	0.29305	0.7200	21.1	0.3650	0.4	Yellowish-white
Strontium	Sr	800-850	...	87.63	2.54	4.03	...	0.0033	...	1.8	White, shining
Tantalum	Ta	2900	...	181.5	10.8	0.0301	0.0800	6.85	2.3	White
Tellurium	Te	452	1390	127.5	6.25	0.0525	0.1680	4.66	...	0.0040	Silver-white
Thallium	Tl	302	1280	204.0	1.88	0.0326	0.3021	5.56	...	0.0046	0.1528	1.8	Dark grey
Tin	Sn	231.9	2270	118.7	7.3	0.0559	0.2234	7.66	Steel-grey
Titanium	Ti	1800	...	48.1	3.59	0.1125	...	31.3	31.5	0.0036	...	6.5-7.5	Silver-white
Tungsten	W	3400	4000	184.0	18.77	0.0336	0.0444	20.0	0.35	...	Light-grey
Uranium	U	<1850	...	238.2	18.7	0.0280	Bluish-white
Vanadium	V	1720	...	51.0	5.5	0.1153	0.0040	0.2653	2.5	...
Zinc	Zn	419.4	930	65.37	7.0	0.0935	0.2918	18.60	29.3

Melting points—Bureau of Standards Circular No. 35.

Boiling points—Collected

of Ductile Tungsten = 18.9

Values are then reciprocals of the resistances of a 1-cm. cube at 0°C.

We may state, broadly speaking, that metals in the pure state are not in their best condition for ordinary service, and yet we shall see that there are important exceptions to this statement. Metals in order to be utilized on any scale must permit being made up into commercial shape and must be sufficiently stable, mechanically or chemically, to insure satisfactory usage throughout normal life under service conditions. It is due to the necessity for improving certain of the properties of metals that small amounts of other metals are added although it is the properties of the principal metal that are desired. Thus we have small amounts of manganese added to iron and nickel to improve the malleability and ductility and small amounts of copper added to gold and silver to improve the wearing qualities, or we have small amounts of arsenic added to copper to improve the resistance to deterioration at high temperatures and small amounts of antimony added to lead to improve the resistance to chemical action. Carried a step further we have in the necessity, or desirability, of improving the properties of the metals, the principal reason for the extended use of the metallic alloys. These alloys are nothing more than metals whose properties have been deliberately modified by the addition of appreciable amounts of one or more metals.

Many times, however, the desire is to keep the metal in as pure a condition as possible to prevent the rapid deterioration in the important property or properties which would be caused by even small amounts of other substances. Copper which is so extensively used for electrical purposes, zinc which is used in rolled and drawn shapes, and tungsten which is used as lamp filaments, offer examples of metals which are used in a state of comparative purity.

In the present discussion we shall consider both of these two types of "pure" metals and, wherever possible, the limitations which are ordinarily placed on the amounts of other metals or impurities will be given.

Aluminum.¹—Aluminum is produced by electrolyzing a bath of fused cryolite containing Al_2O_3 in solution.² This gives metal which is essentially pure aluminum but which invariably con-

¹ Valuable information on aluminum can be secured from the publications of the Aluminum Company of America. The most thorough discussion of aluminum is *Circular No. 76* of the Bureau of Standards.

² See NISSEN, *Chem. and Met. Eng.*, 1918, Vol. 19, p. 804.

tains small amounts of iron and silicon. The principal uses of aluminum may be summarized as follows:

1. In the manufacture of cooking and other utensils. Aluminum is readily rolled into sheets and further formed into utensils, the principal use of which is in the kitchen. Here, on account of its light weight, it is an exceedingly convenient material to work with, and, on account of its high thermal conductivity, heating is comparatively rapid with less danger of burning. As far as its effect on food products is concerned, it is harmless, although the caustic alkalis corrode it readily.

2. In the manufacture of tubes, shapes, etc. By the same token, aluminum can be drawn into tubes and shapes, in which case it is particularly desirable on account of its light weight, strength and resistance to corrosion.

3. In the manufacture of bronzes, and light metal alloys. Aluminum makes useful alloys with other metals, either as a primary constituent (light metal alloys) or as a secondary constituent (aluminum bronze) which will be considered later. Castings of metal, such as Lynite, containing aluminum as the principal constituent, are now extensively used in the manufacture of automobile and airplane parts.

4. In the manufacture of cables for conducting electricity. Aluminum combines relatively high electrical conductivity and a low specific gravity, on which account it is now extensively used as a metallic conductor.

5. In the aluminothermic process of welding and the manufacture of metals and alloys. Aluminum has a relatively high heat of oxidation, so high that it easily reduces the oxides of many of the common metals. On this account it can be used as a reducing agent of these oxides in the preparation of the pure metals and their alloys. Carbon-free metals and alloys of exceptional purity are made in this way.

6. As a deoxidizer in steel making. The high heat of combustion of aluminum is also made use of in steel making practice, in which case metallic aluminum is added to the bath to complete the deoxidation and to assist in "settling up" the bath. The relatively impure metal can be used for this work for the principal impurities, iron and silicon, are harmless in the steel.¹

¹ An excellent discussion of the uses of aluminum has been given by SHULL in a paper to the American Institute of Metals, Boston, 1917.

Physical and Mechanical Properties.—Aluminum is both malleable and ductile and is fairly strong, with considerable resistance to corrosion. One of its most remarkable properties is its low specific gravity. Weighing one-third as much as copper, it has nearly two-thirds the electrical conductivity, which gives the ratio of the cross-sections of aluminum and copper cables of equal conductivity as 1.59 : 1. Aluminum has been extensively used as a substitute for copper in dynamo construction, where its light weight and the protective coating, which serves as an insulator for low potentials, combined with low cost (in Germany) are special advantages (Richter). One of the disadvantages of aluminum as cables for conducting electricity is the high coefficient of expansion¹ which causes excessive sagging in hot weather. This has now been overcome by making cable with a steel core. In order to increase the conductivity of rolled and drawn aluminum it may be annealed, but this treatment impairs the strength. In one case the conductivity was found to increase 10 per cent. by annealing for one hour at 230°C.²

The tensile strength of cast aluminum is 13,500 to 15,500 pounds and of drawn aluminum is from 33,500 to 67,000 pounds, depending upon the amount of work done. The elastic limit is 6,750 to 9,000 pounds for castings and up to 33,500 pounds for wire.³ According to Baumann,⁴ the tensile strength at 100°C. is three-fourths, at 200° two-fifths, and at 300°, one-fourth of its value at 20°C. assuming a value of 13,000 to 21,000 pounds to start with. The modulus of elasticity has been given as about 9,800,000 pounds per square inch.⁵ Aluminum is a comparatively soft metal, its Brinell number (500 kg.) being about 25 and its scleroscope number, with the soft hammer, being about 5. Cold work increases the scleroscope number to about 15.

Annealing Cold-Rolled Aluminum.—In commercial practice cold rolled aluminum sheets are annealed in order to soften them and to remove internal strains (two to five hours at 350 to 500°C., Seligman and Williams; twenty-four hours at 370°C., Anderson;

¹ BRISLEE, *Trans. Faraday Society*, 1911, Vol. 7, p. 221. For hard drawn aluminum = 2.432×10^{-5} .

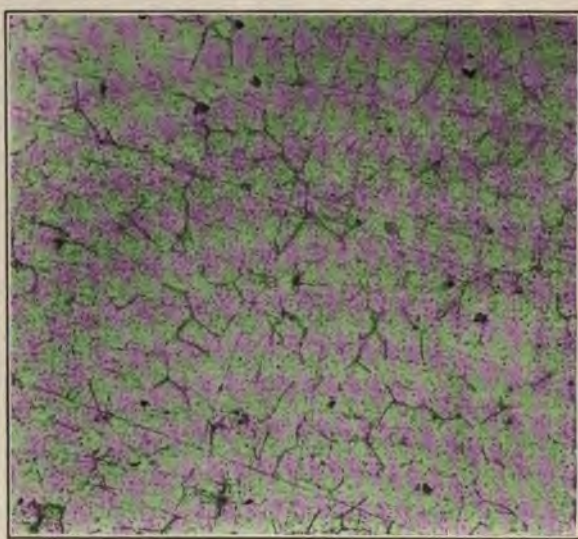
² GEWECKE, *Electrician*, Vol. 72, p. 450. The metal contained 98.82 per cent. Al, 1.041 per cent. Si, and 0.61 per cent. Fe.

³ Metal Industry Handbook.

⁴ *Zeit. Ver. deutsch. Ing.* 1911, Vol. 55, p. 2016.

⁵ BRISLEE, *Trans. Faraday Soc.* 1913, Vol. 9, p. 155.

eighteen to thirty hours at 375° to 400°C., Bureau of Standards). This reduces the Shore scleroscope number from about 15 to about 4 or 5, with the ordinary hammer (Anderson). Equally satisfactory results evidently can be obtained by much less prolonged heatings at slightly higher temperatures, *e.g.*, five to sixty minutes at 475°C.¹ Carpenter and Taverner² have shown that one hour's annealing at 400°C. is sufficient to soften cold-rolled aluminum and to lower the tensile strength from 24,000 pounds to 14,000 pounds per square inch and to raise the elongation (on three inches) from 8 per cent. to 38 per cent.



× 100

FIG. 2.—Aluminum ingot—99 per cent. Al; etched with 0.1 per cent. NaOH. (Bureau of Standards.)

Chemical Properties.—A fresh surface of aluminum exposed to the atmosphere forms a thin protective coating of oxide and then corrodes but little further. Aluminum is highly resistant to the common acids (except those of the halogens), salt water and CO₂, but is readily attacked by caustic alkalies and mercury salts. On account of its electro-positive character, it should

¹ ANDERSON, *Journ. Inst. Met.*, 1918, No. 2, p. 203; In *Met. and Chem. Eng.*, 1918, Vol. 18, p. 712, the same author discusses the metallography of aluminum and methods of preparing sections for microscopic examination. See also, *Journ. Frank. Inst.*, Jan., 1919.

² *Journ. Inst. Metals*, 1917, No. 2, Vol. 18, p. 115.

not be placed in contact with any of the common metals when exposed to the action of water or of dilute acids.

In an extensive investigation of the corrosion of aluminum ware, Heyn and Bauer¹ found that cold worked aluminum, as compared to annealed aluminum, corrodes very badly and they suggested annealing as a means of eliminating the effect. The rate of corrosion is considerably accelerated with rise in temperature, as in cooking. The work of Heyn and Bauer was largely confirmed by Bailey² who pointed out in particular that corrosion is accelerated by the presence of impurities, particularly copper and sodium. The effect of atmospheric corrosion on cold drawn aluminum sections in dirigible balloon and air-plane construction has not been contributed, to the writer's knowledge, although it is known that considerable work has been done on methods of protecting aluminum articles from corrosion.

Impurities in Common Aluminum.—The principal impurities in common aluminum are iron and silicon. In ordinary pure aluminum, iron runs about 0.15 per cent. and over, and the silicon about 0.30 per cent. and over, with the metallic aluminum about 99.35 per cent. Poorer grades run as low as 96 per cent. in aluminum. These impurities can be seen under the microscope as filling matter between the grains of relatively pure aluminum; see Fig. 2. This extraneous material is elongated in the direction of rolling in aluminum sheets or other cold worked material.³

Antimony.⁴—Pure antimony is sold on the market as "star antimony," which designation is a mark of purity. The name comes from the dendrites left standing in relief on the surface of the ingot when the metal solidifies undisturbed in shallow molds. The principal use of antimony is in the manufacture of alloys, such as type metal, bearing metals, hard lead, solder and Britannia metal. It contains, as impurities, small amounts of lead, tin, copper, iron, and arsenic with an antimony content of about 99.75 per cent.

Allotropy.—Antimony occurs in several unstable modifications

¹ *Mitt. k. Materialprüfungsamt.*, 1911, Vol. 29, p. 2.

² *Journ. Inst. Metals*, 1913, No. 1, p. 79.

³ The most complete discussion, with bibliography, on aluminum and its alloys is given in *Circular No. 76* of the Bureau of Standards and should be consulted for more extensive and detailed information.

⁴ For general reference, see WANG, "Antimony," 1909.

but no enantiotropic transformations are known. The least stable variety is yellow antimony which does not possess a single metallic characteristic. An "explosive" variety can be made electrolytically, which reverts to the stable phase with the generation of considerable heat. Another variety, which is black, is produced from the vapor.¹

Bismuth.—There is little use for metallic bismuth except in type metal and in fusible alloys. Bismuth, in wire form, is also used to determine the strength of magnetic fields by reason of the variation of its electrical resistance when in and when out of the field. According to Cohen and Moesveld,² the ratio varies with different samples and depends on the manner of cooling and the structure of the metal. They determined the ratio Y/Y' as 1.20 for bismuth discs and 1.04 for powder, where Y is the specific resistance in a field of 5400 c.g.s. units and Y' is the normal specific resistance. These authors also reported an enantiotropic transformation point at 75°C. (which is doubtful).

Cadmium.—Cadmium, in stick form, resembles tin very closely. It is chiefly used for making fusible alloys and certain aluminum solders. It is also used as a protective coating for other metals. The allotropes of cadmium have been examined by Cohen and Helderman³ who report three, the $\alpha = \beta$ transformation occurring at 65°C.

Cerium.—The most notable property of cerium is that of forming with such metals as iron and copper, easily oxidizable alloys—the pyrophoric alloys. The flame of burning cerium exceeds that of magnesium in brilliancy. Lanthanum, praseodymium and neodymium are very similar to cerium.

Cobalt.—Cobalt resembles the metals iron and nickel very closely, which would be expected from its position in the periodic system. The properties of cobalt are now quite well known but there does not seem to be any considerable use for the metal, at least at the present prices. Its principal use is in the manufacture of high speed steel and "Stellite."

¹ According to COHEN and BOSCH, antimony has a transformation point at 100°C. as shown by the dilatometer, but the work is generally held to be unreliable.

² *Chem. Weekblad*, 1913, Vol. 10, p. 656.

³ *Verslag. Akad. Wet.*, 1913, Vol. 22, p. 420.

Pecheux has given the following properties of cobalt,¹ to which have been added certain determinations of Kalmus and Harper.²

TABLE 2.—PROPERTIES OF COBALT AND NICKEL

	Cobalt		Nickel	
	Pecheux	Kalmus	Pecheux	Kalmus
Melting point.....	1467°C.	1444°C.
Density, 15°C.....	8.8	8.81 (14.5°)	8.8	
Hardness—Mohs.....	5.5		3.5	
Hardness—Brinell ¹		124 (cast)		83 (cast)
Specific heat ²	0.104	See below.	0.108	
Elec. res., 0°C ³	5.5	8.96 (18°)	6.4	
Temperature coefficient ⁴	0.0055		0.0061	
Tensile strength, lbs. per sq. in.....	71,000	34,000 (cast) 61,000+0.3 per cent. C.	60,000	
Yield point.....		App. tensile strength		
Ductility.....		Low for pure Co, higher with C.		

¹ Carbon up to 0.37 per cent. does not seem to increase hardness.

² 10° to 890°C., specific heat = $0.1058 + 0.0000457t + 0.000000066t^2$.

³ Microhms per centimeter cube.

⁴ Between 0° and 20°C.

By measuring the thermal e.m.f. against copper, Stifler found molecular transformations at 280° and 55°C.³

The magnetic transformation of cobalt was given in Fig. 84, p. 190 of Part I.

Copper.⁴—Copper, due to its high conductivity for electricity and its useful mechanical properties, ranks next to iron as the second most important metal. It has a characteristic, reddish color, varying from “orange red to rose color” with the temperature of the cooling water in which it is quenched, although on the fractured surface its color is yellowish.⁵ Copper is obtained in the native or free state from the mines of the Lake Superior District, when it is known as “Lake Copper,” or from

¹ *Compt. Rend.*, 1908, Vol. 147, p. 532.

² *Journ. Ind. Eng. Chem.*, 1914, Vol. 7, p. 6. See also “The Physical Properties of Metallic Cobalt,” Mines Branch *Report*, 1914, which is a very complete treatise on the properties of metallic cobalt.

³ *Phys. Rev.*, 1911, Vol. 33, p. 268.

⁴ For a thorough and authoritative treatise on copper, see *Circular No. 73* of the Bureau of Standards.

⁵ BENNETT, *Met. Chem. Eng.*, 1912, Vol. 12, p. 298.

the sulphide ores of the west, by smelting and electrolytic refining, when it is known as "electrolytic copper." If the smelted copper does not contain gold and silver in sufficient amounts to pay for their recovery, the metal is used directly after fire refining for making alloys. This copper is known as "casting copper."

Copper crystallizes in the isometric system and readily forms twin crystals. Its crystalline structure was found by W. L. Bragg, by means of the X-ray spectrometer, to be simple with a cubic space lattice.¹

Allotropy of Copper.—Copper was thought at one time to be allotropic² but it has recently been shown by Benedicks that the supposed allotropy was really due to copper oxide and copper acetate.³ More recently Cohen and Helderman, in their studies on allotropy, reported a change in the coefficient of expansion at 71.7°C. by dilatometric measurements. This effect was interpreted as being caused by an allotropic transformation and on such a basis a theory was advanced that metals consist of two or more allotropic forms, each of which is characterized by a certain molecular structure. At room temperature, due to incomplete transformation, a metal is generally in the metastable condition, and consists of a mixture of the two forms in varying amounts. According to this hypothesis, the properties, depending on the relative amounts of the two forms which are present, would be, within certain limits, variable or indeterminate.

This "supposed" allotropy of copper has since been refuted by the results of very accurate measurements of the electrical resistance, which was found to vary uniformly and continuously between 0° and 100°C.⁴ The very important conclusion was drawn that ordinary copper is not in a metastable state at room temperature.

Physical Properties.—Copper resembles gold and silver in its physical properties. It is highly malleable and ductile and can be drawn into wire, and rolled into rods or shapes and sheets. In common with other metals, its properties undergo profound changes under such treatment, a fact which must be borne in

¹ *Phil. Mag.*, 1915, Vol. 28, p. 355.

² SCHUETZENBERGER, *compt. Rend.*, 1887, Vol. 86, pp. 1240 and 1597.

³ *Metallurgic*, 1907, Vol. 4, p. 5.

⁴ BURGESS and KELLBERG, *Journ. Wash. Acad. Sci.*, 1915, Vol. 5, p. 21.

mind when considering the physical properties. Another point of vital importance here is the effect of temperature on the physical properties of copper, all of which will be considered somewhat in detail in the following. Inasmuch as the "history" of the material determines, in a large measure, the incidental physical and mechanical properties, values of these properties will be given later.

The electrical conductivity of copper is often expressed in terms of the Matthiessen Standard which is 100 for copper which has a resistance of 0.141729 ohms per meter-gram or a specific resistance of 1.594 microhms per centimeter cube at 0°C. Wolff and Dellinger concluded that the best value for the "Annealed Copper Standard" is 0.153022 ohm per meter-gram at 20°C.¹ Other standard values are reproduced in Table 3.

TABLE 3.—ELECTRICAL RESISTANCE OF PURE COPPER

Temperature. °C.	Resistivity	α for annealed wire	α for hard-drawn wire	Density
0	0.1411	0.00428	0.00415	8.90
15	0.1500	0.00402	0.00391
20	0.153022 ²	0.00394	0.00383	8.89
25	0.1560	0.00386	0.00376

Resistivity is given in ohms per meter-gram.

α = temperature coefficient.

$$\alpha_{20} = \frac{R_t - R_{20}}{R_{20}(t - 20)} \text{ etc.}$$

Commercial copper which is used for electrical purposes is remarkably uniform, irrespective of the kind of copper and of the source, and shows consistently high results.³ Electrolytic copper, if anything, has a slightly higher conductivity than Lake copper. As a standard value we may take that adopted by the

¹ *Bull.* Bureau of Standards, 1911, Vol. 7, No. 1. *Reprint* No. 148.

² This resistivity is equivalent to 1.72128 microhms per cm. cu. at 20°C. or a conductivity of 5.8096(10⁻⁴) c.g.s. units at 20°C.

³ This refers to electrolytic or Lake copper in the cast and drawn condition. Cast copper used for electrical purposes has a much lower conductivity but Comstock has shown that by deoxidizing with silicon, a conductivity of 75 to 85 per cent. of that of copper wire can be secured. *Trans. Amer. Electrochem. Soc.*, 1919, Vol. 32, p. 220.

International Electro-Technical Congress (San Francisco) in 1915, for annealed copper, of 0.017241 ohms for a wire one meter long and a cross section of one square millimeter at 20°C. ($d = 8.89$). The change in resistance per degree Centigrade (between 10° and 20°) was assumed to be 0.000068 ohm. This standard gives a value of 62.9 for the conductivity of copper in Table 1.

Values of the resistance of copper at elevated temperatures and the change in resistance on melting have been determined by Northrup¹ whose results are given in Table 4.

TABLE 4.—RESISTANCE OF PURE COPPER AT HIGH TEMPERATURES

	microhms/cm. cu.
20°C.	1.7347
1000°C.	9.42
1083°C.—solid	10.20
1083°C.—liquid	21.30
1100°C.	21.43
1340°C.	23.39
1450°C.	24.22

The Effect of Mechanical Work.—The effect of varying degrees of cold work on soft or annealed copper has been determined for a series of rods drawn from various diameters to No. 12 B. & S. and then tested for conductivity and tensile strength.² In this way it was found that, by reducing the area by 80 per cent., the conductivity was lowered to about 98 per cent. of its original value, while the tensile strength was increased from about 35,000 pounds to nearly 58,000 pounds per square inch. The first reductions were the most active in “hardening” the copper. In Fig. 3 are shown the mechanical properties of copper cold drawn by various amounts.³ Certain values obtained by Alkins are also inserted.

More recently Mathewson and Thalheimer⁴ repeated these tests using electrolytic copper and two grades of Lake copper, one of them containing 0.296 per cent. arsenic. In general, the behavior of the three grades of copper was the same, although the effect of cold work was more pronounced on the arsenical

¹ *Journ. Frank. Inst.*, 1914, Vol. 177, p. 1.

² ADDICKS, *Electrochem. Ind.*, 1903, Vol. 1, p. 581.

³ GRARD, *Proc. 6th Congress Intern. Assoc. Test. Mater.*, New York, 1912, *Paper II*, 15.

⁴ *Trans. Amer. Inst. Min. Eng.*, 1917, Vol. 55, p. 446.

copper than on the electrolytic copper, with the non-arsenical Lake copper occupying an intermediate position. According to the work of Alkins, the effect of drawing annealed copper rod cold from 0.553 inch to 0.0403 inch in twenty-five passes, is to increase the tensile strength from 34,500 pounds to 67,000 pounds per square inch. This was also checked by Johnson who experimented with cold rolled copper. The elongation fell from 57.8 per cent. for annealed copper (gage length = $4\sqrt{\text{area}}$) to 7.8 per cent. for a reduction of 89 per cent., beyond which point the elongation

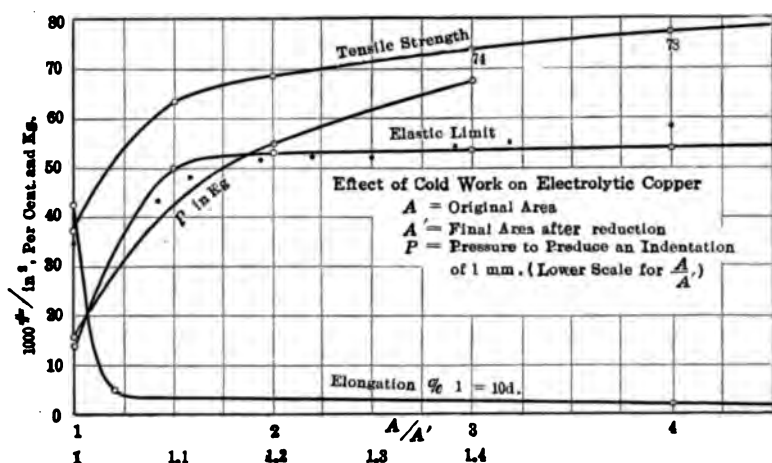


FIG. 3.—Properties of cold-worked copper. (Grand.) Values plotted (·) give tensile strengths as determined by Alkins on material with 99.97 per cent. copper and 0.02 per cent. oxygen.

remained essentially the same.¹ An interesting point under investigation was the anomaly which occurred at about 50 per cent. reduction. At this point a further reduction of nearly 25 per cent. is without effect on the tensile and other properties.

Two methods are in use for checking the "hardness" of cold worked or drawn copper, Brinell hardness and grain size determinations, but at least one metallographist has advised using the microscopic method as giving a more reliable index and being more general in its application.² Present practice with brass shows that the Brinell test is the more generally useful of the two and the same might well hold here.

¹ ALKINS, *Journ. Inst. Met.*, 1918, No. 2, p. 33, and 1920, No. 1; JOHNSON, *Ibid.*, 1919, No. 1, p. 335.

² GUILLET, *Rev. de Met.*, 1915, Vol. 12, p. 819.

Annealing Copper.—In common with other metals, hard drawn copper becomes soft or annealed by heating to moderately low temperatures. The temperature required decreases somewhat as the time of exposure increases and is lower for pure copper than for copper containing impurities. Some values obtained by Grard are reproduced in Fig. 4. These show that an anneal at 250°C. (time not given) is sufficient to “anneal” the copper he used, and that annealing at temperatures above 700°C. produce marked deterioration. Curves given by Heyn in his *Materialienkunde IIA* to show the effect of annealing on the resistance and grain size are reproduced in Figs. 5 and 6. The deleterious effect of “over-annealing” was followed by Heyn¹ by means of

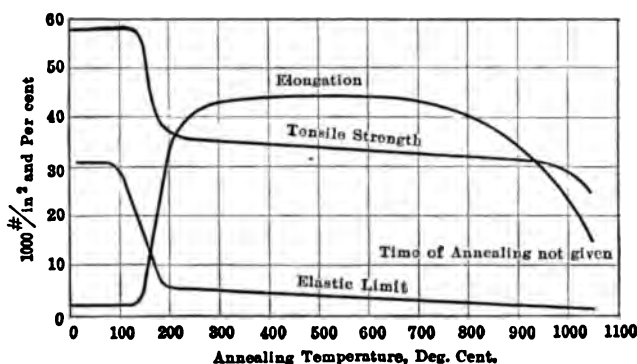


FIG. 4.—Effect of annealing hard drawn copper. (Grard.)

his bend test on unnotched bars. The bending number of annealed copper (from 30 min. to 30 hrs. at 500°C.) was found to be $6\frac{3}{4}$. Annealing a few minutes at 1000°C. was sufficient to produce brittleness and a bending number of only 4. Annealing at temperatures just below the melting point was found to “burn” the copper, by absorption of oxygen as Cu_2O . The brittleness produced in copper by annealing at moderately high temperatures, and which is commonly referred to as “burning,” has been shown to be due to deoxidation,² although this action must result in the formation of a gas, such as H_2O .³ The effect of oxygen on the annealing of copper was further considered by Caesar and Gerner who found that Cu_2O produces a marked softening

¹ *Materialienkunde IIA*, p. 310.

² RUDER, *Metal Industry*, 1916, Vol. 14, p. 209.

³ PILLING, *Journ. Frank. Inst.*, 1918, Vol. 186, p. 373.

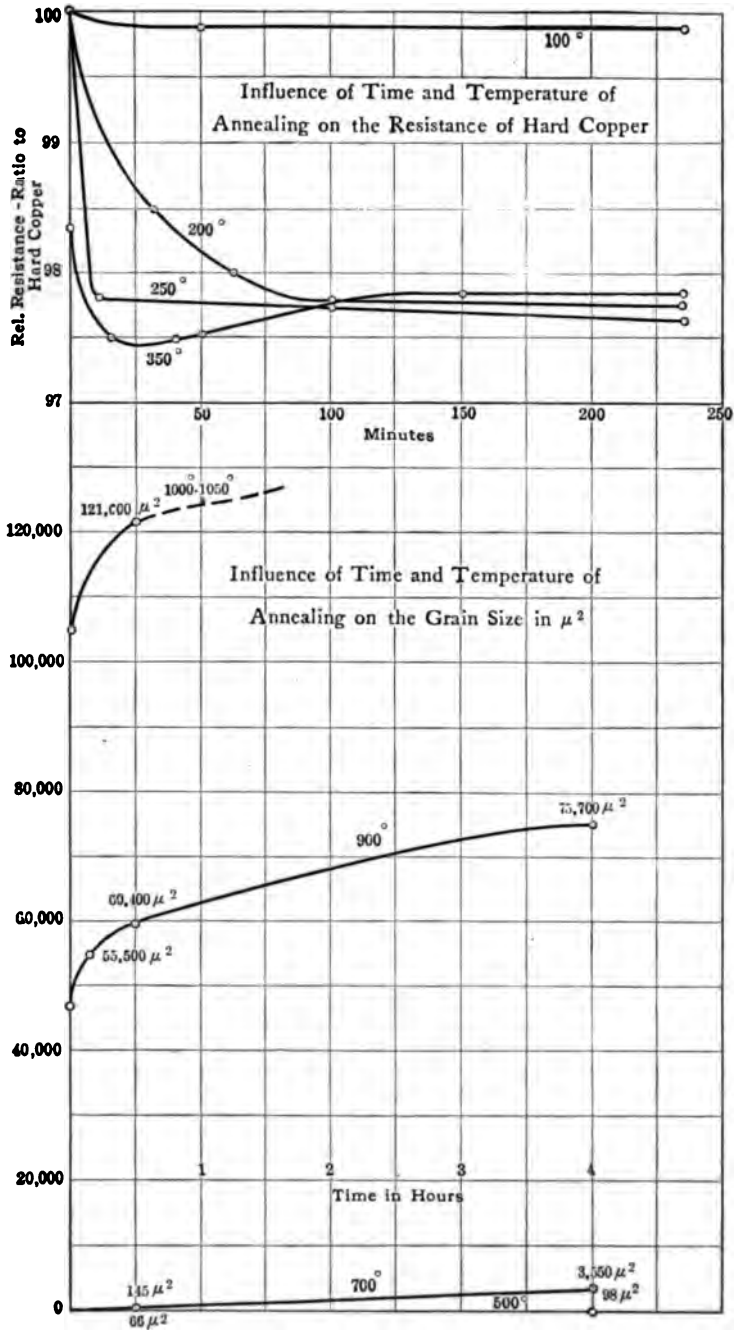


FIG. 5.—Time and temperature effect on annealing hard drawn copper. (Gewecke.)

effect in that it produces the change from the hard to the soft state at a lower temperature. This effect is opposed by silver, which raises the softening range, so that copper with 0.002 per cent. silver and 0.08 per cent. oxygen behaves approximately the same as pure copper.¹ The softening of hard drawn copper apparently is not accompanied by any marked dilatation effect.²

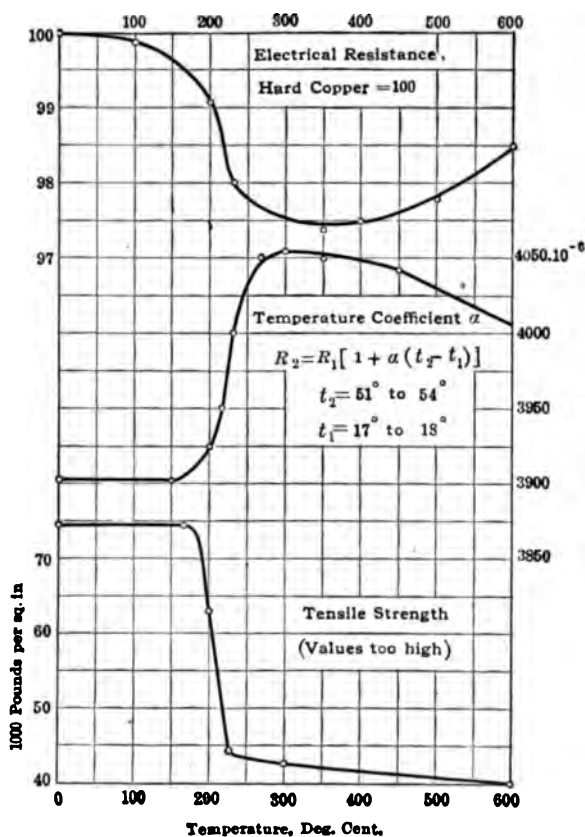


FIG. 6.—Effect of annealing on the electrical properties of hard drawn copper. (Gewecke.)

As a chemical means of distinguishing between cold drawn and annealed copper, Heyn found the most reliable index to be relative solubilities of hard drawn copper and the same annealed 20 min. at 550°C., in a 5 per cent. KCN solution. The relative

¹ *Trans. Am. Soc. Mech. Eng.*, 1916, Vol. 38, p. 838.

² TURNER and LEVY, *Journ. Iron and Steel Inst.*, 1906, No. 1, p. 48.

dissolution of the hard drawn copper, in 24 hours, was found to be 61, assuming that of annealed copper to be 100.

As a rule, the notched bar impact test is not used on copper but Baucke has used the method to distinguish between tough copper and brittle copper, particularly that which contains oxygen or which has been heated at relatively high temperatures while exposed to the furnace gases. He found a comparatively low impact figure for cast copper and a maximum value, after forging to about $\frac{1}{5}$ the original thickness, of 25 to 30 mkg. Oxygen was found to reduce the figure to about $\frac{1}{3}$ its normal value. Bismuth, in small amounts, and arsenic and antimony in somewhat larger amounts, also make copper brittle. The opposite effect is produced by nickel, tin, zinc, manganese, and aluminum. Hydrogen was found to be particularly harmful in the presence of oxygen, due probably to the formation of water vapor at a high pressure during forging.

Mechanical Properties at High Temperatures.—The tensile properties of copper at high temperatures have been reported on by a number of observers, but their results are not as conclusive as might be desired.¹ An increase in temperature causes a decrease in strength for all grades of copper, irrespective of their purity or physical condition. The decrease is gradual at first, but more rapid at higher temperatures, varying with the material. Hard copper retains its superior strength up to the "softening temperature," but not above. Copper, which possesses higher tensile strength due to impurities (such as tin), retains its superior strength over pure copper, although the difference is not so great at high temperatures.

The effect of temperature on ductility is not so clear. According to Rudeloff and A. Le Chatelier,² and Huntington, the ductility drops rapidly above 200° to 300°C., as if there were a breaking down or softening point at that range. This was also verified by Guillet and Bernard³ who found a maximum fragility, as determined by the resistance to shock, for copper and many of its alloys at 300° to 400°C. On the other hand, experiments

¹ See RUDELOFF, *Proc. Int. Soc. Test. Mater.*, Copenhagen, 1909, *Pape VI-1*, p. 18; BENGOUGH, *Journ. Inst. Metals*, 1912, No. 1, p. 123; HUNTINGTON, *Ibid.*, 1912, No. 2, p. 126; BENGOUGH and HANSON, *Ibid.*, 1914, No. 2 p. 56; HUNTINGTON, *Ibid.*, 1915, no. 1, p. 23.

² *Congress Int. d. Met. d'Essen*, 1901, Tome 2.

³ *Compt. Rend.*, 1913, Vol. 156, p. 1899.

by Rudeloff and Bengough indicate no lowering of the ductility at that point, but a sudden and pronounced increase at 500° to 600°C. This behavior can not be explained as due to a difference in the rate of loading as Stribeck, by loading very slowly, obtained high elongations at low temperatures, a sudden loss in ductility at 250° and low elongations at 650°.

Electrolytic Copper.—Electrolytic copper, like cast copper, is crystalline but to just what extent the laws governing the crystallization of a solid metal, as considered in Part I, can be applied to the electrodeposition of copper, is not clear at present. Certain it is, however, that the solid phase, on being deposited, has a marked tendency to crystallize and to form crystallites of a size and character which depend largely on the conditions of the electrodeposition. Faust¹ has shown that increasing the current density and lowering the concentration of copper in the electrolyte, decreases the size of the crystallites. Von Schwarz has shown, on the other hand, that crystals up to 5 cm. or more in length can be deposited by carefully avoiding agitation and by keeping the temperature at or near 0°C.²

In general, referring now to the copper sulphate electrolyte, we may say that increasing the current density results in a finer grained and stronger copper, provided that the current density is not so high that "burnt" copper is produced. By replenishing the supply of copper at the cathode by agitation, the permissible current density is greatly increased. We may also state that raising the temperature results in a coarser deposit, but that higher temperatures permit the use of higher current densities. The tensile strength of the copper varies with the fineness of the deposit.³

The possibility of depositing copper in the amorphous state under the conditions just stated is not known to the writer. This leads to an interesting point in connection with the amorphous phase theory, inasmuch as electrodeposited copper can be made extremely strong and hard. The elastic limit of electrodeposited copper is 9,500 lbs. in the direction of growth of the

¹ *Zeit. anorg. Chemie*, 1912, Vol. 78, p. 201

² *Intern. Journ. Metallography* 1915, Vol. 7, p. 124; or *Journ. Chem. Soc.*, 1916, Vol. 110, II, p. 34.

³ BLUM, HOLLER and RAWDON. *Trans. Amer. Electrochem. Soc.*, 1916, Vol. 30, p. 159. BLUM., *Ibid.*, 1919, Vol. 36. These statements are in general agreement with Prof. Bancroft's axioms.

crystallite (= direction of maximum conductivity) and 9,700 lbs. in a direction at right angles, as compared to 2,900 lbs. of melted and slowly cooled copper.¹ Bennett has shown that by keeping the temperature below 75°F. and by rapidly rotating the cathode and increasing the current density, a tensile strength equal to that of "hard-drawn" copper (68,000 lbs.) can be secured.² To explain this by the amorphous phase theory, it would be necessary to assume a (local) deformation equivalent to that produced during severe cold working, a deduction which would hardly be justified.

The occurrence of twinned octahedra was noted by von Schwarz and discussed at length by Rawdon³ who observed that twinning results from the side pressure of neighboring crystals sufficient to produce "rotation," but that twinned crystals, in themselves, do not have any noticeable effect on the mechanical properties. It has been shown that a change in the conditions of deposition in the direction which produces finer deposits, changes the structure from a coarse columnar structure to a fine columnar structure which is fairly well broken up, to a structure which is completely broken up and characterized by twinning. These latter structures accompany the higher tensile strengths and are converted into an "equiaxed" and coarser structure by annealing (two hours at 610°C.). Annealing also "softens" the hard electrodeposited copper.

Impurities in Copper.⁴—Refined copper has been very thoroughly discussed by Addicks in a paper which is valuable for general reference.⁵ As a representative analysis, he gives—copper plus silver, 99.931 per cent.; oxygen as the chief impurity, 0.040 per cent.; and several thousandths each of sulphur, iron, nickel, arsenic, antimony, aluminum and lead.

Impurities are classified by the refiner into (1) those which depress the conductivity—such as arsenic, (2) those which impair the ductility—such as lead, tellurium and bismuth, and (3)

¹ FAUST: This was considered by FAUST to be due to electrical forces during electrolysis which often produce internal strains.

² *Met. Chem. Eng.*, 1912, Vol. 10, p. 298.

³ *Met. Chem. Eng.*, 1916, Vol. 15, p. 406.

⁴ A very thorough but brief discussion of copper, the effect of impurities and the more important alloys is given by HOFMAN, *Metallurgy of Copper*, 1914, which has been freely consulted in the present discussion.

⁵ *Journ. Amer. Inst. Met.*, 1914, Vol. 8, p. 161.

those which are of value if reclaimed—such as gold, silver, platinum and palladium. The elements which lower the conductivity can be kept under control by the conductivity test. The principal impurities present in commercial copper are lead, which has an inappreciable effect when below 0.010 per cent., oxygen, which affects the strength, toughness and annealing properties, and arsenic.

As the most important impurity in copper we have oxygen which is introduced during melting, as copper readily absorbs oxygen at temperatures just below the melting point and above. On this account it is necessary to use deoxidizers (see Part III) in order to reduce the amount of oxygen to about 0.5 per cent. Cu_2O , in which form it occurs, which amount is needed in order to retain the other impurities in the form of oxides. In the oxide form, impurities are much less harmful than if in the metallic state.¹ Cu_2O and copper form a eutectic at 3.4 per cent. Cu_2O which melts at 1063°C .² Up to about 0.5 per cent. Cu_2O , oxygen has an inconsiderable effect on the mechanical properties, but above that composition it “hardens” copper.

Effect of Lead.—The amount of lead which can be present and not affect the mechanical properties of copper, depends somewhat on the other impurities present. Hofman sums up this point as follows. The less the oxygen, the smaller is the amount of lead permissible, because lead reduces the copper oxide.³ Thus oxygen-free copper with 0.05 per cent. lead is red-short, while oxygen-bearing copper can stand as much as 0.2 per cent. and be worked hot or cold. Jolibois and Thomas have shown that arsenic neutralizes the harmful effect of lead as lead forms a solid solution with Cu_3As .⁴ Ordinarily it is held that lead, not to exceed 0.1 per cent., makes copper roll better, and that 0.2 per cent. makes it brittle.⁵ Archbutt, on the other hand, has

¹ A microscopical method of determining the amount of oxygen in copper, both rapidly and accurately, has been developed, the modification due to BARDWELL (*Bull. Amer. Inst. Min. Eng.*, 1913, No. 79, p. 1429) probably being the most satisfactory for technical practice.

² See *The Metallographist*, 1903, Vol. 6, p. 49; or *Trans. Amer. Inst. Min. Eng.*, 1904, Vol. 34, p. 677.

³ JOLIBOIS and THOMAS, *Rev. de Mét.*, 1913, Vol. 10, p. 1264.

⁴ *Loc. cit.*

⁵ See *Engineering*, 1903, Vol. 76, p. 753; *Engineering and Mining Journ.*, 1904, Vol. 77, p. 284; *Mining Industry*, 1903, Vol. 12, p. 127; *Met. Chem. Eng.*, 1912, Vol. 10, p. 540.

shown that 0.2 per cent. lead does not necessarily interfere in forging at a red heat.¹

Effect of Arsenic.—Arsenic is a very important impurity on account of the large amount of arsenical copper used. Arsenic forms an arsenide Cu_3As which first enters into solid solution in copper up to about 4 per cent. and then forms a eutectic at 78.5 per cent. copper, which melts at 684°C .²

The exact effect of arsenic on copper is still a matter of dispute, but that a certain amount (up to 0.5 per cent. As) added to copper which is to be used at elevated temperatures and in harmful gases, such as for staying locomotive fire boxes, is beneficial, is without question. Johnson has pointed out the functions of arsenic in copper to be the following: (1) to lower the susceptibility of copper for gases and thus confer soundness and toughness; (2) to neutralize the ill effects of lead and bismuth; (3) to make it better withstand elevated temperatures; and (4) by disseminating the copper oxide, to improve its cold working properties.³ According to Muntz, on the other hand, the only object of adding arsenic is as a deoxidizer and, furthermore, that such a function can be better accomplished by silicon, aluminum or phosphorus, which are less apt to produce occluded gases. The experience obtained in engineering practice seems to point favorably toward arsenical copper although that does not mean that some other addition would not better serve the purpose than arsenic.

The practice of adding iron and silicon to improve the properties of arsenical copper and to secure sound ingots, has been discussed by Johnson, who gives the properties and structures of various alloys of this class.⁴

From the tensile tests reported, it is evident that 0.5 per cent. arsenic increases the tensile strength of copper about 10,000 lbs. and the elongation by 20 per cent. of the elongation of pure copper.⁵

¹ *Journ. Inst. Metals*, 1912, No. 1, p. 265.

² See FRIEDERICH, *Metallurgie*, 1908, Vol. 5, p. 529; and BENGOUGH and HILL, *Journ. Inst. Met.*, 1910, No. 1, p. 34.

³ *Journ. Inst. Metals*, 1913, No. 2, p. 275.

⁴ *Loc. cit.*

⁵ See LEWIS, *Jour. Soc. Chem. Ind.*, 1901, Vol. 20, p. 254; 1903, Vol. 22, p. 1351. LEWIS, *Met. Chem. Eng.*, 1912, Vol. 10, p. 540. JOHNSON, *Journ. Inst. Metals*, 1910, No. 2, p. 163; 1912, No. 2, p. 192; 1913, No. 2, p. 275. BENGOUGH and HILL, *Journ. Inst. Metals*, 1910, No. 1, p. 37. GREAVES, *Journ. Inst. Metals*, 1912, No. 1, p. 218; HIORNS and LAMB, *Jour. Soc. Chem. Ind.*, 1909, Vol. 28, p. 451.

Effect of Antimony.—Antimony, while seldom an ingredient of copper, has much the same effect as arsenic, but is considerably less desirable. It forms a compound Cu_3Sb which is soluble in copper up to about 8 per cent. antimony.¹ As much as 0.3 to 0.4 per cent. increases the hardness and is held to improve the

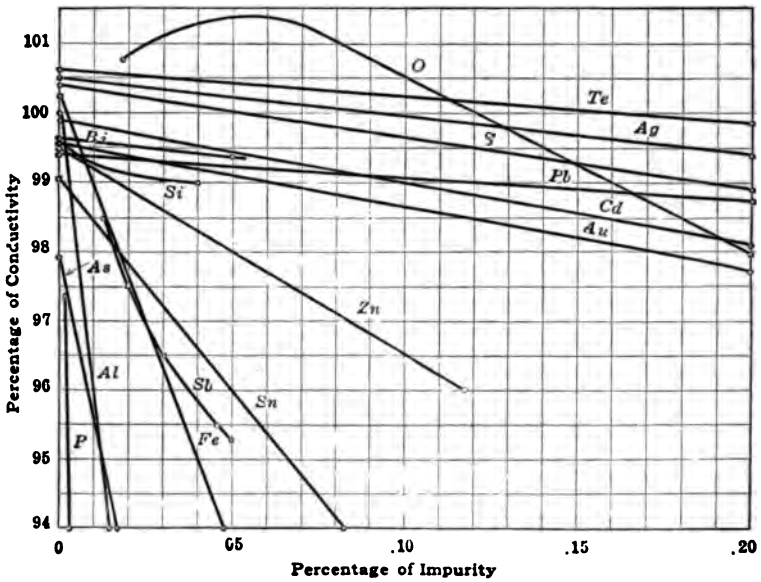


FIG. 7.—Effect of impurities on the conductivity of copper. (Addicks.)

general mechanical properties, while if copper contains 0.05 per cent. bismuth, antimony should be added as a corrective measure.²

The effect of the principal impurities on the conductivity of copper was very thoroughly worked out by Addicks whose results can best be reproduced by means of the curves in Fig. 7.³

¹ See CARPENTER, *Intern. Journ. Metallography*, 1913, Vol. 4, p. 300. Iron, when present, makes copper hard and brittle. For the effect of P, Mn and Zn on the conductivity and mechanical properties of Cu, see MÜNKER, *Met.*, 1912, Vol. 9, p. 185, and for the effect of gases, see STAHL, *Met.*, 1907, Vol. 4, p. 761. An important article dealing with copper intended for use as locomotive fire boxes has appeared recently; see OBERHOFFER, *Met. u. Erz*, 1918, Vol. 15, p. 47. In this work, the influence of heating to the temperature of rolling, the temperature of rolling, and rolling proper, on the mechanical properties and microstructure were investigated. The material analyzed Cu 99.46 per cent.; Sn 0.11 per cent.; As 0.231 per cent.; and O 0.11 per cent.

² STAHL. *Metall u. Erz*, 1918, Nov. 8.

³ *Trans. Amer. Inst. Min. Eng.*, 1906, Vol. 36, p. 18.

Hardening Copper.—There have been frequent but unsuccessful attempts made to revive the “lost art” of hardening copper and to produce a material, as the ancients are supposed to have done, with cutting properties approaching those of steel. When summed up, those processes consist in (a) alloying some element or elements with copper, or (b) mechanically working copper in some way or another, or (c) a combination of these two methods. The only “secret” or patentable part of the process is in the method or material employed, and it may be said that, to a certain extent, some of the methods suggested have been successful.

Certain selected specifications of commercial copper are reproduced from the year book of the American Society for Testing Materials, 1915.

TABLE 5.—SPECIFICATIONS OF COMMERCIAL COPPER. A. S. T. M., 1915

	Diam., inches	Tensile strength in 1000 lb. per sq. in.	Elongation, per cent.	Electric resistance 20°C., lb. per ohm-mile
Hard-drawn.....	0.460	49	3.75 in 10"	900.77
Hard-drawn.....	0.040	67	0.85 in 60"	910.15
Medium hard-drawn	0.460	42-49	3.75 in 10"	896.15
Medium hard-drawn	0.040	53-60	0.88 in 60"	905.44
Annealed.....	0.460	36	35.00 in 10"	891.58
Annealed.....	0.003	40	20.00 in 10"	891.58

Specific gravity taken as 8.89 for calculations.

Equivalent resistances

lbs. per ohm-mile	891.58	896.15	900.77	905.44	910.15
Microhms per cm. cu...	1.7564	1.7654	1.7745	1.7837	1.7930

Gold.—Gold, like copper, possesses a very characteristic color—golden yellow. When finely divided it is reddish purple, while molten golden and gold leaf, by transmitted light, are green. It is the most malleable and ductile of all the metals. Pure gold melts at 1063°C. and begins to volatilize at 1100°C. It has a very small tendency to absorb gases when molten.

Gold possesses the lowest solution pressure of the common metals and may be precipitated from solution by even the weakest reducing agents, such as hydrogen, phosphorus, arsenic, antimony and carbon, except from cyanide solution, from which it can be precipitated only by strongly electro-positive elements such as zinc.

The resistivities of pure gold at temperatures from 20° to 1500°C. have been determined by Northrup¹ and are given in Table 6.

TABLE 6.—RESISTIVITY OF PURE GOLD
Microhms per cc.

20°C.	2.3166
300°C.	4.72
500°C.	6.62
800°C.	9.94
1000°C.	12.54
1063°C.—solid	13.50
1063°C.—molten	30.82
1100°C.	31.34
1200°C.	32.76
1300°C.	34.17
1400°C.	35.58
1500°C.	37.00

Annealing of Gold.—A very thorough account of the annealing of gold has been given by T. K. Rose of the Royal Mint, London.² By “annealing temperature” was meant the lowest temperature at which rolled gold is completely softened in 30 minutes. For pure gold, this temperature is 150°C. For gold plus various impurities, it was found to be as follows: for 0.05 per cent. silver, 225°C.; for 0.05 per cent. copper, 250°C.; for 0.002 per cent. hydrogen, over 300°C.; for 8.33 per cent. silver, 450°C. Amounts of impurities as small as 0.001 to 0.002 per cent. can be detected in this way. Pure gold is completely recrystallized by thirty minutes annealing at 150°C., while impure gold, after a similar treatment, shows the original laminated structure.

Unlike the base metals, there is no danger from oxidation during melting although the reducing gases may be taken up to some extent. Pure gold melted in hydrogen is reduced in purity from 1000.00 fine to 999.96 fine, and the annealing temperature is raised thereby to 300°C. By remelting in oxygen, the gold is brought back to nearly its original condition. Rose suggests adding 0.1 per cent. CuO to molten gold, during melting, to oxidize and eliminate the impurities.

Iridium.—Iridium is insoluble in acids and aqua regia and is now being employed as a constituent of alloys intended to

¹ *Journ. Frank. Inst.*, 1914, Vol. 177, p. 287.

² *Journ. Inst. Metals*, 1913, No. 2, p. 150; see also PHELPS, *Journ. Inst. Metals*, 1914, No. 2, p. 125.

be used as substitutes for platinum. The pure metal is drawn into tubes and used for resistors in electric furnaces, which purpose it serves extremely well. It is also used with ruthenium as a thermocouple for measuring high temperatures but it does not remain constant for any appreciable time and the couple must be frequently checked.

Iron.—Iron is by far the most commonly used metal, without which, it may be said, the recent progress in engineering would have been impossible. This remarkable utility of iron is due principally to three things, not necessarily independent: (1) iron is the strongest of the common metals, and possesses at the same time great ductility and toughness; (2) iron forms useful alloys either with carbon alone or with carbon and other elements such as nickel, manganese, chromium, etc.; and (3) iron exists in at least two allotropic forms, the behavior of which towards carbon (or Fe_3C) gives rise to the possibilities of "heat treatment," by which the most remarkable combinations of properties can be secured. Without the transformation which occurs in steel, it is highly doubtful if steel would find any general application, either in the slowly cooled or "heat treated" condition, and engineers would be limited to such metals as pure iron, brass, bronze, iron-nickel alloys, etc. On account of the great significance, both scientific and technical, attached to this allotropy of iron, the question has received more than the usual amount of attention and we shall now consider it somewhat in detail.

Allotropy.—While we cannot here, in any sense, enter into a discussion of the historical development of this subject, it is well to know that the various physical manifestations accompanying the changes in iron (and steel) have been the subject of scientific investigation for well over a half of a century and that, as early as 1890, Osmond came to the conclusion that "iron is a polymorphous element."¹ Proceeding to a brief statement of the allotropy of iron, it may be said that iron is allotropic on account of the structural change, and the accompanying physical phenomena, produced when the pure metal is allowed to heat up or cool down through 900°C . It has also been advanced that the magnetic and thermal disturbances at 767°C . are also indications of allotropy in iron. These two points are indicated in the nomenclature of iron, *e.g.*, iron up to 767°C . is called α iron

¹ "On the Critical Points of Iron and Steel," *Journ. Iron and Steel Inst.*, 1890, No. 1, p. 38.

and is strongly magnetic; iron between 767°C. and about 900°C. is called β iron and is but very weakly magnetic; and iron above 900°C. is called γ iron. More recently another modification of iron has been discovered which is stable from 1401°C. to the melting point and is called δ iron.¹ Following Osmond, the transformations or "critical points" have been called A_2 at 767°, Ac_2 on heating and Ar_2 on cooling, and A_3 at 900°, Ac_3 on heating and Ar_3 on cooling. In this, A stands for arrêt = arrest, c for chauffage = heating and r for refroidissement = cooling. A_1 stands for a third point, not found in pure iron, and will be discussed under "steel."

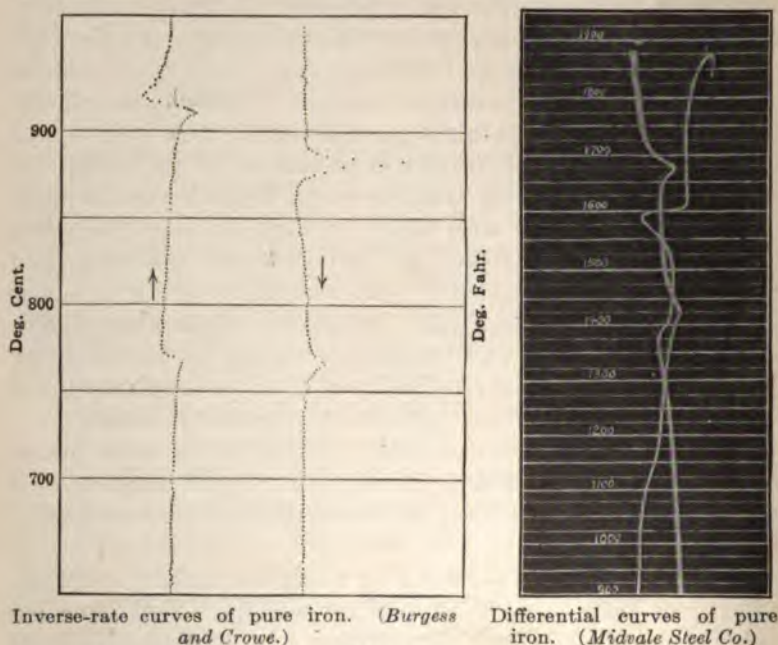


FIG. 8.

Thermal Analysis.—The temperatures of the critical points, both A_2 and A_3 , may be readily determined by thermal analysis. A differential curve of pure ingot iron, as determined photographically by the Le Chatelier-Saladin apparatus at the Midvale Steel Company, is reproduced in Fig. 8. A curve for electrolytic iron recorded by Burgess and Crowe is also reproduced.²

¹ RUER and KLESPEER, *Ferrum*, 1914, Vol. 11, p. 258.

² *Scientific Paper* No. 213, Bureau of Standards.

The curves of Burgess and Crowe were recorded with the greatest accuracy and the authors regard it as "proved beyond a reasonable doubt that under standard conditions there is a definite transformation at 768°C. and a less defined although more intense one at 898° to 909°C. in terms of their maxima on cooling and heating." There can now be no reasonable doubt that the curves in Fig. 8 represent the true thermal effects in pure iron.¹

Magnetic Changes at the Critical Points.—Variation in magnetism with temperature also offers a very useful means for studying the allotropy of iron, thus Hopkinson has shown a drop in permeability from 11,000 at 775° to 1 at 785° for a field strength

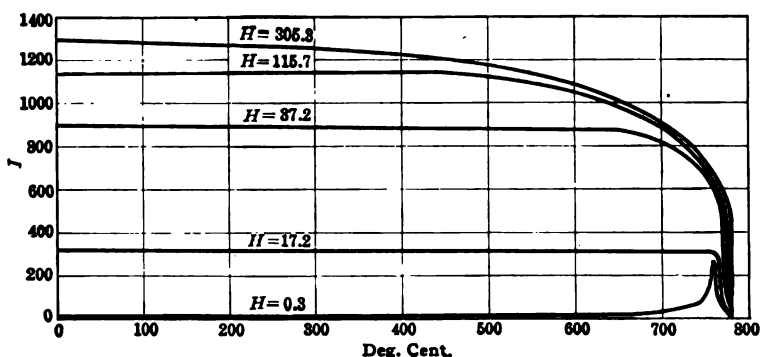


FIG. 9.—Effect of temperature and field strength on the intensity of magnetization of iron. (Collected.)

of 0.3.² This phenomenon can also be followed, though somewhat more crudely, by heating a bar of pure iron while it is within the field of a magnetic needle and noting that at a low red heat, the iron suddenly loses its power to attract the needle. This effect is the "magnetic transformation" at the A_{c2} point, about which there has been so much controversy. The very interesting effect of the field strength on the magnetic transformation has been shown by P. Curie³ whose results are given in Fig. 9.

¹ A double thermal point at A_2 was described by OSMOND, and again more recently by ARNOLD, but it is held that such a "doubling" certainly can not be truly indicative of the thermal effect at this point, at least not for standard conditions. Heating and cooling curves repeatedly secured in the writer's laboratory confirm the shapes of the critical point curves shown in Fig. 8.

² Phil. Trans., 1889, Vol. 180, p. 443.

³ Ann. Chim. et Phys., 1895 (4), Vol. 5, p. 280.

This work shows that it is only in low field strengths that the transformation occurs at a definite temperature. More recent work has shown that the curves in Fig. 9, while sufficiently exact for ordinary purposes, do not give the correct idea of the A_2 transformation; thus, Honda has shown that the loss of ferromagnetism, when followed by a sensitive method, is continuous, although when magnetometrically measured, that it occurs at a well-defined temperature.¹ The change in magnetism with temperature at the A_3 and A_4 points is given in Fig. 10. At A_3 , the change is sudden and well-defined, as contrasted with the change below A_3 . While these measurements were being made the temperature was changing at an "extremely slow rate."

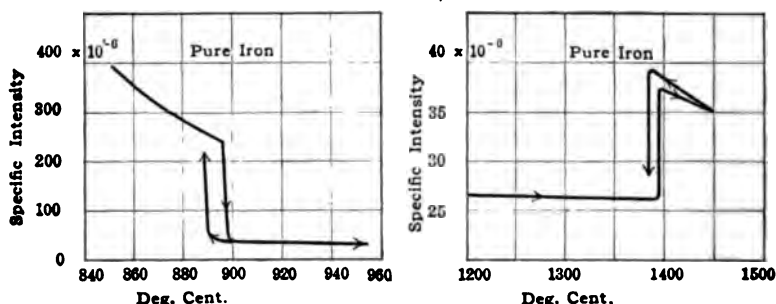


FIG. 10.—Magnetic transformations at A_3 and A_4 . (Ishiwara.)

It might be thought that the curve for low field strengths is more truly typical of the A_2 transformation and that increasing the strength of the field, which might act as another variable, would extend the transformation over a range of temperature. If such were so, it would follow that the thermal heat effect would likewise be extended over a range of temperature. This point was also investigated by Honda who determined the effect of a magnetic field on the heat effect at A_2 by recording heating and cooling curves of pure iron both in and out of a strong magnetic field. The magnetic field was found to have no effect in

¹ "Nature of the A_2 Transformation in Iron," *Journ. Iron and Steel Inst.*, 1915, No. 1, p. 199. This paper contains a very thorough, although condensed, review of the properties of iron, steel, nickel and cobalt, and their bearing on the magnetic and allotropic phenomena in these metals. In a recent paper he again discusses the A_2 point and contributes curves of Ishiwara which are reproduced in the text. *Ibid.*, 1919, No. 1, p. 457.

displacing the thermal critical point, as it did the magnetic transformation, showing that there is no definite relation between the two effects. In the same way, Honda determined the magnetization and electrical resistance simultaneously and found that the transition at point "m" in Fig. 11 coincides with the loss of ferro-magnetism.

Changes in Electrical Resistance at the Critical Points.—The resistance of pure iron (99.98 per cent. Fe) has been followed by a number of investigators, but the work of Burgess and Kellberg¹ is given here, as they used, for their work, an extremely

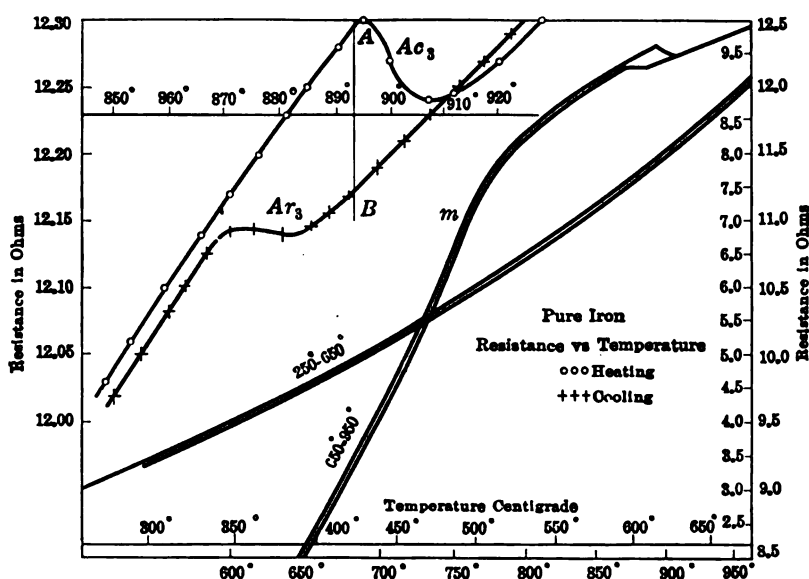


FIG. 11.—Resistance—temperature curves of pure iron. (Burgess and Kellberg.)

accurate and sensitive method. Their Fig. 2, which is reproduced here—Fig. 11—shows the transition at A_2 and the break at A_3 . The change at A_3 follows the general law that the denser state is the better conductor. According to this law, and the shape of the curve at A_2 , we should expect a change in the variation of the specific volume with temperature (i.e., a transition on the specific volume-temperature curve), but not a discontinuity, at A_2 .

¹ *Scien. Paper*, No. 236, Bureau of Standards, 1914.

Dilatation at the Critical Points.—Benedicks, who determined the dilatation of pure iron by an extremely sensitive method,¹ one which was capable of measuring lengths with an accuracy of 8×10^{-6} per cent., found the dilatation in strict accordance with the R- θ curve, *i.e.*, a transition at A_2 and a discontinuity at A_3 . One of his curves is reproduced in Fig. 12.²

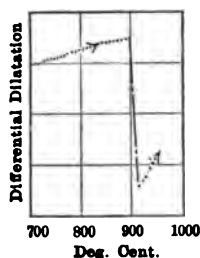


FIG. 12.—Dilatation of pure iron. (Benedicks.)

Changes in Thermal E.M.F. at the Critical Points.—Measurements of the thermal e.m.f. of pure iron also serve to bring out the critical points and it may be said that the results agree with those found by other methods. The most recent, and probably the most accurate, of the results of this kind are



FIG. 13.—Thermal E. M. F. curves of pure iron. (Burgess and Scott.)

¹ *Journ. Iron and Steel Inst.*, 1914, No. 1, p. 419.

² Other workers who have recorded the dilatation of iron are notably—BRONIEWSKI, *Compt. Rend.*, 1913, Vol. 156, pp. 699, 1983; ROSENHAIN and HUMFREY, *Proc. Roy. Soc.*, 1909, Vol. 83, p. 200; LE CHATELIER, *Compt. Rend.*, 1890, Vol. 129, pp. 279, 331. BENEDICKS made a few observations of the magnetostriction at various temperatures, but beyond bringing out the upper limit of ferro-magnetism, nothing was gained thereby.

those of Burgess and Scott,¹ whose results are given in Fig. 13. These curves show the customary transition and lack of hysteresis at A_2 and the break and hysteresis at A_3 .²

Calorimetric Determinations.—The amount of heat involved in the changes at A_2 and A_3 has been measured by means of the ice-calorimeter, by Meuthen, and found to be 5.6 and 14.1 calories per gram respectively for iron containing 0.06 per cent. C.³ This checks the results of thermal analysis which always show a greater heat effect at A_3 than at A_2 .⁴ Meuthen located the critical points between 770° and 790°, and 880° and 900°C. respectively.

Changes in the Mechanical Properties at the Critical Points.

The mechanical properties of pure iron at elevated temperatures have been very skillfully determined by Rosenhain and Humfrey, who showed, beyond doubt,

a discontinuity at A_3 , the denser phase (γ) possessing the greater strength by about 4,000 pounds per sq. in.⁵ The variation at A_2 is less indicative of a definite transformation point, as can be seen from their results which are reproduced in Fig. 14.

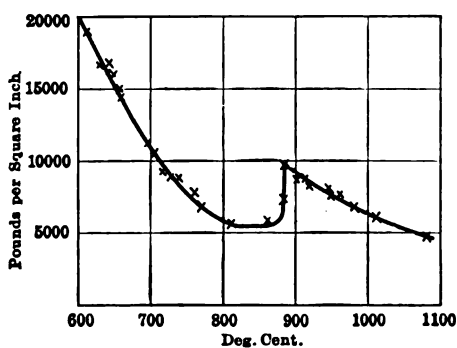


FIG. 14.—Tensile strength of iron at high temperatures. (Rosenhain and Humfrey.)

¹ *Compt. Rend.*, 1916, Vol. 163, p. 30; *Journ. Iron and Steel Inst.*, 1916 No. 2, p. 258.

² A thermo-electric effect is produced by moving an iron wire through an electric furnace which is heated above 900°C. by "thermo-electric hysteresis" and BENEDICKS has shown by this means that the A_3 point may be brought out. *Compt. Rend.*, 1916, Vol. 162, p. 297, and *Journ. Iron and Steel Inst.*, 1916, No. 1, p. 211. See also *Met. and Chem. Eng.*, 1916, Vol. 15, p. 337.

Other important work on the thermo-electric behavior of iron is as follows: HARRISON, *Phil. Mag.*, 1902, No. 6, Vol. 3, p. 177; BELLOC, *Ann. Chim. et Phys.*, 1903, Vol. 30, p. 42; and BRONIEWSKI, *Compt. Rend.*, 1913, Vol. 156, pp. 669, 1983.

³ *Ferrum*, 1912, Vol. 10, p. 1.

⁴ See the calculations of OSMOND, *Compt. Rend.*, 1886, Vol. 103, pp. 743, 1135, (1.3 cal. at A_2 and 3.8 cal. at A_3 in steel with 0.16 per cent. C); and of STANSFIELD, *Journ. Iron and Steel Inst.*, 1899, No. 2, p. 169 (1.0 cal. at A_2 and 2.86 cal. at A_3).

⁵ *Proc. Roy. Soc.*, 1909, Vol. 83, p. 200 and *Journ. Iron and Steel Inst.*, 1913, No. 1, p. 219.

Crystallography of Iron.—In an early paper on the "Crystallography of Iron," Osmond stated that iron, in all forms, crystallizes in the cubic or isometric system, γ generally in octahedra, and α and β in cubes, there being no difference, crystallographically, between α and β .¹ A summary of this work is given in the following table.

TABLE 7

	αFe	βFe	γFe
Planes of translation.....	$a^1(111)$ difficult	None known	$a^1(111)$ easy
Mechanical twinning, planes of twinning.....	$a^1(111)$	None known	$a^1(111)$
Mechanical twinning, planes of junction.....	$a^1(112)$	None known	$a^1(111)$
Twinning by annealing, planes of twinning.....	None known	None known	$a^1(111)$
Twinning by annealing, planes of junction.....	None known	None known	$a^1(111)$
Face of maximum hardness.....	$a^1(111)$?	$b^1(011)?$
Planes of easiest etching	$p(001)$	$p(001)$	$p(001)$

In a later publication (with Cartaud), which is the most comprehensive treatise we have on the subject,² further work on the crystallography of iron was contributed. As the result of this work the authors drew the "positive conclusion" that "the three allotropic varieties of iron, although they all crystallize in the same cubic system, present well-marked specific characters, and cannot have the same internal structure," but it would seem necessary to reconsider many of the points in the light of the more recent determinations of the physical properties. Better still would be the measurement of the space lattice at the temperatures in question by X-ray analysis.

Rosenhain and Humfrey adduced further evidence, which was held to support the allotropic theory of Osmond, by straining iron strips, which had been heated differentially along the length, sufficiently to produce slip bands and twinning. By microscopical examination of a strained strip of electrolytic iron, commencing at

¹ The *Metallographist*, 1900, Vol. 3, p. 275.

² *Trans. Amer. Inst. Min. Eng.*, 1906, Vol. 37, p. 813; and *Journ. Iron and Steel Inst.*, 1906, No. 3, p. 444.

the cold end and passing toward the hot portion (ca. 1100°C.), it was noted that the extent of the "slipping" increased up to a certain well-defined point, at which place visible evidence of plastic deformation ceased. This point is well illustrated by Fig. 14. With further increase in temperature, "slipping" and "twinning" became profuse again but were of a different character from that produced at the lower temperature ranges, and resembled the known twinning of γ iron in alloy steels which is produced in them by deformation at ordinary temperatures—see Fig. 15. Taken in connection with the results shown in Fig. 12,

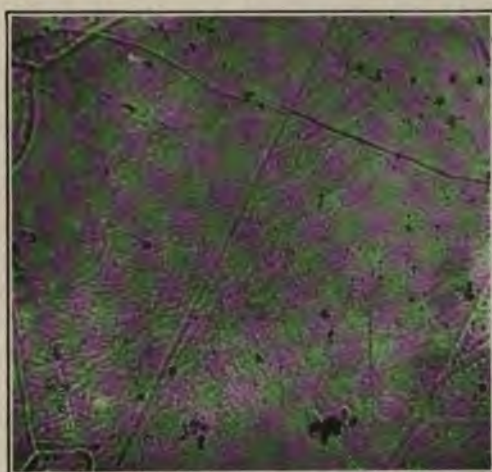


FIG. 15.—Twinning in gamma iron. Polished surface heated in vacuo above A_{c3} . (Ravedon and Scott.)

and the sudden change in resistance to deformation of Fig. 14 it would appear that the sudden increase in tensile strength must correspond to the A_{c3} point, although the opinion expressed at the time was that this change occurred at the A_2 point and that the change at A_3 left no mark on the differentially heated and strained strip.

The re-crystallization at A_3 is one of the most direct and positive indications of allotropy in iron and has been demonstrated by a number of workers. It is due to this fact that over-heated iron may be "restored" by grain refining, in which respect iron differs from copper and other unimorphic metals. Kroll has shown, in particular, that by heating and cooling through A_3 ,

three superposed polygonal structures are produced, caused, evidently, only by a recrystallization.¹ Two superposed structures are evident in Fig. 15. Stead and Carpenter have shown, by some very refined experiments on electrolytic iron 0.01 inch in thickness, that relatively enormous crystallites may be formed in as short a time as three seconds by passing up and down through A_3 . Once these form, it is impossible to destroy them (by heat treatment) unless heating is continued to above A_3 , in which case, by the process of recrystallization, they are immediately changed into new and smaller crystals. Indeed, in order to explain the phenomena met with, it was necessary to invoke the laws governing the formation of new phases, as laid down by Tammann. All this indicates that the change at A_3 is a definite crystallographic change, or a phasial change. The effect at A_2 , in so far as is now known, is not caused by nor accompanied by any such crystallographic change.²

A general review of the properties and crystallography of iron shows that we have to consider two types of phenomena—a phasial change at A_3 and a temperature effect at A_2 (molecular or atomic) not accompanied by a structural change. On this basis, the transformation at A_3 is truly enantiotropic and the changes in physical properties as well as the thermal effect are reversible, but occur at a higher temperature on heating than on cooling. At A_2 there is no structural change, but in the light of the recent experimental evidence cited above, there is no necessity for assuming one in order to explain the changes. The principal change at A_2 is the magnetic transformation, which is no different in iron than in nickel, cobalt and other ferro-magnetic substances, even as to the accompanying heat effect and change in conductivity. Le Chatelier, in 1905, called attention to this inherent difference between A_2 and A_3 . He pointed out that the A_3 change is similar to the changes in sulphur, phosphorus, etc., i.e., that iron is allotropic or dimorphic, and further, regarding the A_2 effect, that iron loses its magnetism progressively and that the temperature interval over which the loss occurs can not be likened to the retardation or “sluggishness” of the A_3 transformation. It may be presumed that Prof. Le Chatelier had in mind that the properties at A_2 depend solely on the temperature and

¹ *Journ. Iron and Steel Inst.*, 1910, No. 1, p. 304.

² Further evidence of the change at A_3 may be obtained from EWEN, *Intern. Journ. Metallography*, 1914, vol. 6, p. 1.

that the change in properties is due solely to change in temperature, while at A_3 the properties and change in properties depend as well on the phasial conditions. Obviously A_3 can complete itself, once it has commenced, at constant temperature, while A_2 must wait on the change in temperature. Prof. Honda has amplified this discussion, in the paper referred to, and has incorporated this idea into a definition of allotropy. It is of interest to note that Le Chatelier's original conception of the difference between A_2 and A_3 is now being substantiated on all sides by the more recent work, and seems to be rather generally adopted.

We have already noted that the A_3 change occurs at a higher temperature on heating than on cooling, which brings up the hysteresis requirement of allotropy (enantiotropy) a point which has been so urgently insisted upon by Dr. Benedicks. The fundamental difference between A_3 and A_2 , in this respect, has been shown by Burgess and Crowe in their work on the critical points of pure iron. They showed, after careful experimentation, that for a zero rate of heating and cooling, the hysteresis at A_2 was 0° , while that for A_3 was still 12° . In other words, at A_3 the equilibrium temperature *must* be overstepped in both directions before the transformation can proceed. The actual temperature at which it begins will depend on the rate of heating or cooling and will be one corresponding to a nuclei number sufficiently high to initiate spontaneous crystallization. Reducing the rate to zero does not eliminate the hysteresis because the nuclei number itself approaches zero as the equilibrium temperature is approached. A_2 , not involving the formation of a new phase (nuclei), is not subject to hysteresis.

In the present discussion it has not been possible to do full justice to much of the valuable work which has been done on this subject; the aim has been rather to present certain of the facts which have been ascertained which best serve to throw light on that which actually takes place at A_3 and A_2 and to draw what seems (to the writer) to be the logical conclusions regarding the nature of the two points. It is quite true that in certain quarters iron is not even regarded as an allotropic element and Oxley of the University of Sheffield has explained the change in iron at A_3 as a change in the "packing" of the molecules, a contention supported by Sir Robert Hadfield.¹ To this contention,

¹*Trans. Faraday Soc.*, 1916, Vol. 11, p. 125.

the logical answer seems to be that the birth of new crystals in the old crystals (recrystallization) and hysteresis are the results only of a phasial or two phase, allotropic, transformation. At A_2 we have neither recrystallization nor hysteresis and consequently it is not assumed that A_2 is an allotropic change but rather that it is associated with molecular or atomic phenomena.

The Physical Properties.—The density of pure iron may be taken as 7.85 to 7.87. Benedicks has shown that the increase in specific volume for one per cent. of various added elements is as follows: Mn 0.00006; P 0.00089; Si 0.00117; C 0.0018; Al 0.0025, positive in each case. The thermal coefficient of expansion is given by Le Chatelier as follows: 0.000011 at 0°C ., 0.000017 at 785°C ., and 0.000015 above 900°C .

The electrical resistance of pure iron is given as about 9.0 microhms per centimeter cube at 0°C . or 10.08 at 20°C . This figure was determined to be 7.6 at room temperature, by Benedicks, who calculated it by extrapolation from the resistances of various steels, on the assumption that equal atomic percentages increase the resistance by equal amounts. He gave as the formula,

$$\sigma = 7.6 + \Sigma C'$$

where $\Sigma C = C' + 12.0/28.4 \text{ Si} + 12.0/55.0 \text{ Mn} + \dots\dots\dots$

Cold work is generally considered to have the effect of increasing the resistance although, as we shall see later, evidence contradicting the statement has been advanced.

The strong (ferro-) magnetism of iron is one of its most remarkable properties and one which suits it for a number of important technical uses, such as for transformer cores, parts of motors and dynamos, electro magnets, etc. Iron which is to be used for the latter purposes should have a high permeability, which may be secured by using a pure grade of iron and subjecting it to suitable heat treatment (annealing). Of these two expedients heat treatment is of greater importance than the impurities which are generally found in commercial iron. Annealing materially improves otherwise low-grade material by making iron magnetically softer and promoting uniformity.¹ The correct annealing temperature naturally varies with the results which must be accomplished but they do not seem to have been intelligently worked out, which applies particularly to transformer sheets.

¹ TERRY, *Phys. Review*, 1910, Vol. 30, p. 133.

Evidently the small amounts of gases and impurities in commercial iron have a considerable effect in lowering the permeability for it has been shown that iron of exceptional purity has a much higher permeability; for example the permeability of vacuum-fused electrolytic iron was found to be 19,000 for a flux density of 9,500 gauss. The average hysteresis loss was less than 50 per cent. of that found in the best grade of transformer steel, on account of the extremely low coercive force.¹ The permeability of wrought iron has been given by McAllister as

$$\mu = 2800 - 3.2 \frac{(7500 - B)^2}{10^6} \text{ for } B_0 = 15,000$$

The Mechanical Properties.—Pure iron or the purest commercial soft steel may be said to have the following properties: tensile strength, 40,000 lbs.; elastic limit, 20,000 lbs.; elongation, 50 per cent., where gage length divided by cross sectional area equals 8; reduction of area, 84 per cent.² Soft iron is very tough and in the form of wire will stand a great amount of twisting and bending, which suits it for binding wire. It is in its toughest condition when at 35°C., according to Goerens and Hartel.³ At -75°C. iron is very fragile, while again at a blue heat it is also in a comparatively brittle condition and should not be severely worked while at that temperature. The author is informed by private communication that some very excellent properties can be induced in iron (and steel) by suitable working at "blue heat," but as yet there has been little contributed on the subject. Lantz found that iron at 320°C. has only one-fifth the ductility which it has at room temperature.⁴ Copper wire, tested at the same time, was found to stand less bending than iron wire. Soft annealed iron is only 20 points harder on the Brinell scale than annealed copper.⁵

Corrosion.—The general subject of the corrosion of iron will be left for discussion in Part III, suffice it to say here that pure iron, in all its forms, corrodes or rusts. Gases and impurities, in general, are held to be harmful and it is common experience that the poorer grades of Bessemer steel rust more

¹ YENSEN, *Bull. Univ. Ill. Eng. Expt. Stn.*, No. 83, 1915.

² STEAD, *Journ. Iron and Steel Inst.*, 1916, No. 2, p. 5.

³ *Zeit. anorg. Chem.*, 1913, Vol. 81, p. 130.

⁴ *Stahl u. Eisen*, 1915, Vol. 35, p. 22.

⁵ KELLEY, *Met. Ind.*, 1919, Vol. 14, p. 61. Pure electrolytic iron can be softened to 83 B. H. by annealing for one hour at 1050°C.

rapidly than more refined steel. Among the more resistant materials of commerce are wrought iron, a pure iron made in the open hearth furnace, known as American Ingot Iron, and copper-bearing steel. In an investigation conducted by the writer, copper-bearing steel (0.15 per cent. C; 0.20 per cent. Cu) resisted atmospheric corrosion better than any other common sheeting material. Next in order came pure open hearth iron and then open hearth steel and Bessemer steel.

Richards and Behr have made the interesting observation that the electrolytic potential of iron is unaffected by stress, even up to the breaking stress.¹ In this respect iron behaves differently from copper and its alloys.

Passivity.—By placing iron in concentrated nitric acid or in potassium bichromate solutions, iron can be made “passive” so that it is not acted upon by the ordinary corroding agencies. There are two views regarding the passivity of iron, one that iron is ordinarily active but is made passive (noble) by the presence of oxygen in some form, and the other that iron is ordinarily passive and is made active by hydrogen.²

Electrolytic Iron.—Müller has described the production of electrolytic iron using a sulphate electrolyte.³ He noted that the sulphate solution used always left a little sulphur in the iron, about 0.006 per cent. He showed, as had been demonstrated by Roberts-Austen and others, that the critical points were well defined and at their proper temperatures as soon as the hydrogen was removed by annealing. Amberg showed that by using a chloride solution, much less sulphur and nitrogen are absorbed.⁴ This practice seems to be followed at present.⁵

¹ *Zeit. physikal. Chem.*, Vol. 58, p. 301.

² This question has been very thoroughly discussed by HEATHCOTE, *J. Soc. Chem. Ind.*, 1907, Vol. 26, p. 899.

³ *Metallurgie*, 1909, Vol. 6, p. 145.

⁴ *Zeit. Elektrochem.*, Vol. 10, p. 125.

⁵ Other experimenters have reported their methods of preparing electrolytic iron and the precautions necessary. See BURGESS and HAMBUECHEN, *Iron and Steel Mag.*, 1904, Vol. 8, p. 48. Improvements were discussed by WATTS and LI, *Amer. Electrochem. Soc.*, Apr. 18, 1914. STORY described the methods used at Wisconsin, *Trans. Amer. Electrochem. Soc.*, 1914, Vol. 25, p. 489, and YENSEN at Illinois, *Bull. Eng. Expt. Stn., Univ. of Ill.*, No. 72, 1914. At Wisconsin, American Ingot Iron was used as the source of iron and the electrolyte was an aqueous solution of FeSO_4 and NH_4Cl , with a current density of 10 amp. per sq. ft. Typical analyses of “refined” and “doubly refined” iron were as follows: S 0.001 and 0.000; Si 0.003 and 0.013;

American Ingot Iron.—A very pure iron, called ingot iron, is now made in the open hearth furnace by a process which is not essentially different from basic open hearth practice. It is believed that the "boiling" or oxidation period is continued longer, while the temperature is held quite high, to reduce the impurities. This treatment results in a highly oxidized bath which is then treated with ferro-silicon instead of the customary ferromanganese, and finally a small amount of aluminum is added to complete the degasification. The analysis is supposed to show 99.84 per cent. metallic iron with 0.010 C; 0.025 Mn; 0.005 P; 0.005 Si; 0.025 S; 0.050 Cu; 0.004 Ni; 0.001 H; 0.035 O;

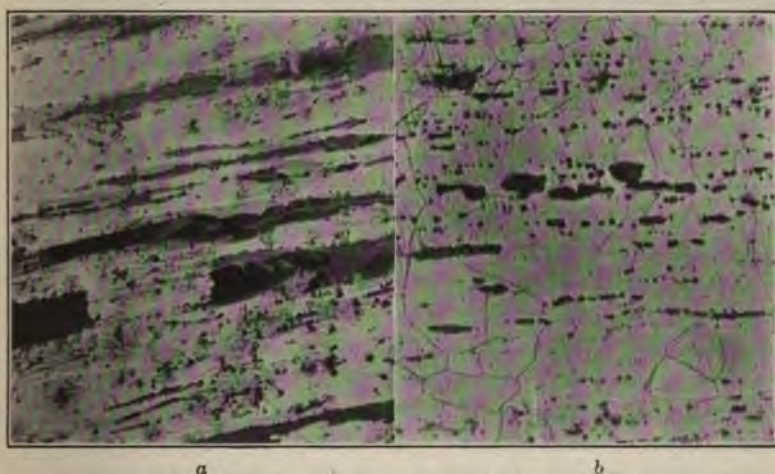


FIG. 16.—Wrought iron. *a*—unetched; *b*—etched.

total impurities 0.160 per cent. The useful properties of this ingot iron are said to be increased resistance to corrosion, high electrical conductivity, high permeability and low residual magnetism and good mechanical properties.

Wrought Iron.—Wrought iron is a relatively pure grade of iron made by "puddling" pig iron. The iron always contains a

P 0.020 and 0.004; C 0.013 and 0.012; H 0.083 and 0.072; Mn 0.000 and 0.000.

CAIN, SCHRAMM and CLEAVES have described the method at the Bureau of Standards used to make iron with 99.974 per cent. Fe; *Scientific Paper* No. 266. A 25 to 30 per cent. solution of FeCl_2 was the electrolyte. The microstructure of electrolytic iron is given in the last two papers. In all cases it was necessary to heat to above A_c to produce recrystallization. The production of electrolytic iron on a commercial scale has been discussed by GUILLET, *Journ. Iron and Steel Inst.*, 1914, No. 2, p. 66.

certain amount of slag, due to the incomplete removal of the furnace slag during the mechanical working of the "ball" and muck bar. An analysis of wrought iron may be taken as follows: C. trace; Mn. trace; P, .05; S, .02; Si, trace. The appearance of wrought iron under the microscope may be seen from Fig. 16. The ferrite occurs as equiaxial crystals and not as elongated "fibres" as is sometimes supposed. The "fibre" of wrought iron obviously is due to the included slag which is elongated in the direction of rolling. The slag stringers show sometimes one constituent and sometimes two. In the latter case one of the constituents frequently shows a dendritic structure and the ground mass, if viewed under a high magnification, is seen to be a eutectic.

Phosphorus produces at times a dangerous segregate which may cause premature failures of the material. This occurrence has been described by Rawdon, who noted streaks of coarsely crystalline, high phosphorus material running longitudinally through the bar.¹ These segregates showed a peculiar mottled appearance on deep etching, which would indicate a non-uniform phosphorus distribution in the individual grains.

Lead.—Lead is the softest of the common metals, the purest lead being the softest. It can be rolled into sheets but is too weak to be drawn into fine wire. Pure lead is used for sheet lead, pipe and other forms of lead and in the manufacture of solder and other alloys. It contains as impurities, in the approximate order of their quantity—antimony, copper, bismuth, iron, silver, zinc, nickel, cadmium, arsenic, cobalt, manganese and sulphur.² These impurities are present in very small quantities as the metallic lead runs 99.96 per cent. and over in the various grades.

Antimony in lead produces the hard lead of commerce. Its effect is to increase the hardness, lower the ductility and increase its resistance to cold acids. On this account, hard lead is used as shot and bullets, and in pumps, valves, and storage batteries, where corrosive liquids are encountered. It has been found that about 3 per cent. of antimony added to lead materially improves the properties of lead cable sheath.

Lead is very sensitive to coalescence, which may be produced by slightly elevated temperatures or by the action of electrolytes.

¹ *Bull. Amer. Inst. Min. Eng.*, 1917, p. 1344.

² COLLINS, "Lead," 1910.

Bauer has shown that the resistance to bending is materially lowered, through increase in grain size, by heating for several days at temperatures above 100°C.¹ The grain growth in rolled lead, as affected by electrolytes, has been shown by Baucke.²

Nickel.—For a discussion of nickel, reference will be made to the excellent contribution of Browne and Thompson, *Bull.* No. 153; American Institute of Mining and Metallurgical Engineers, p. 2693.

Platinum.—Platinum is normally malleable and ductile but is appreciably altered by impurities; thus palladium, rhodium, and iridium harden platinum and lower its ductility, while as little as 0.03 per cent. silicon makes it hard and brittle. Its tenacity lies between that of silver and that of copper. It has a coefficient of expansion of 0.00000907 at 50°C. and of 0.00001130 at 1000°C., which is abnormally low for metals and the same as some kinds of glass. On this account it can be sealed into glass so as to produce tight seal.

Platinum is highly resistant to acids and has a high melting point, consequently it is extensively used for laboratory purposes. It is also used for dental purposes, as standard weights, as sealed-in wires in the manufacture of incandescent lamps, in the electrical industries and in pyrometry. For some reason, which is to be regretted, platinum has gained favor for jewelry purposes so that considerable quantities of the metal are absorbed in that industry, reducing the amount available for scientific purposes.

Platinum can be produced in a very pure state, containing as little as 0.01 per cent. of impurities (Geibel). Analyses which are more typical of commercial platinum are given by Priwosnik.³

	Pt	Ir	Rh	Pd	Ru	Fe	Cu	Total
Pure Pt.....	99.28	0.32	0.13	trace	0.04	0.06	0.07	99.90
Pt crucible.....	96.90	2.56	0.20	trace	0.02	0.20	99.88

The specific conductivity of pure platinum has been given as 9.12×10^4 at 0°C.

There has been considerable work done on the microscopical

¹ *Mitt. kgl. Materialprüfungsamt*, 1913, Vol. 31, p. 357.

² *Int. Journ. Metallography*, 1911-12, Vol. 2, p. 243.

³ *Oest. Zeit. Berg-Huetten.*, Vol. 60, p. 143.

and physical methods of control of the quality of platinum ware, but at this place it will be deemed sufficient (and preferable) to refer to the work of the Bureau of Standards.¹

Silver.—Silver is extremely malleable and ductile although less so than gold. It is harder than gold and softer than copper. It is the most perfect conductor of heat and electricity known. Metallic silver can be produced in a very pure state or with less than 0.005 per cent. impurities, according to Laird and Hulett.² The specific conductivity of electrolytic silver is given as 68.12×10^4 at 0°C. The change in resistivity of pure silver follows the laws which are common to other pure metals and increases as a nearly linear function up to the melting point. At this temperature the resistance increases abruptly from 8.5 to 16.6 microhms per centimeter cube.³

The tensile test brings out the great ductility and lack of strength of pure or "fine" silver. One such test made on silver cast in an iron mold gave an elastic limit of 2500 pounds, a yield point of 5700 pounds and a tensile strength of 15,500 pounds per square inch, and an elongation of 56 per cent. and a reduction of area of 67.8 per cent. The hardness values were about 28.0 to 30.5 with the Brinell test using a 10 mm. ball and a load of 500 kg. and 8 to 12 with the scleroscope using a magnifier hammer. This hardness is increased by cold work but is restored by annealing at 670°C. for 20 to 30 minutes, which is standard works practice.⁴

Pure silver absorbs considerable quantities of oxygen (22 volumes), on being heated above its melting point. This is given off during solidification causing the so-called "spitting." According to Baker, this oxygen is absorbed as an oxide which is stable at high temperatures but which decomposes as the temperature falls.⁵ This effect can be eliminated by adding more easily oxidizable metals or by using a protective cover over the molten silver. Some such expedient is necessary if satisfactory castings are to be had.

A study of the various forms in which silver occurs has been made by Kohlschutter and co-workers, which may or may not

¹ *Scientific Papers* No. 254 (1915) and No. 280 (1916).

² *Trans. Amer. Electrochem. Soc.*, 1912, Vol. 22, p. 345.

³ NORTHROP, *Journ. Frank. Inst.*, 1914, Vol. 178, p. 85.

⁴ SMITH AND TURNER, *Journ. Inst. Met.*, 1919, No. 2, p. 149.

⁵ *Proc. Chem. Soc.*, Vol. 30, p. 56.

be of interest to the metallographist. For reference, a list of the articles is appended.¹

Allotropy of Silver.—Silver is not commonly supposed to be allotropic and it can be safely stated that there are no characteristics traceable to allotropy such as are met with in the case of iron or tin. Recently we have seen a statement of the allotropy of silver from the Utrecht laboratory which places silver in a class with copper and certain other metals which are said to be allotropic.² The experimental evidence is based on the relative specific volume of silver in different conditions of heat and mechanical treatment and the general conclusion drawn is that silver has a transition point at about 77°C. Certain it is that additional and more convincing evidence will have to be advanced before silver will be held as one of the allotropic elements.

Effect of Impurities.—The addition of copper lowers the melting point and makes silver harder without sensibly impairing its malleability or altering its color. Zinc has somewhat the same effect. Cadmium produces softer, whiter, and more ductile and malleable alloys than copper does. Tin makes silver harder and somewhat more brittle. Platinum is added to silver for dental alloys as they are harder and not as readily corrodible as pure silver. Bismuth ordinarily does not dissolve in silver in the solid state so that a very small amount is sufficient to make silver brittle. Annealing for a few hours at 275°C. causes bismuth to pass into solution so that the alloy becomes ductile.³ The addition of copper prevents the bismuth from being dissolved so that bismuth can not be tolerated in silver-copper alloys. Iron and silver are completely insoluble so that silver can be melted down in an iron crucible without danger of contamination. Fine silver is at least 998.0 fine, the remainder being principally copper, iron and lead, with small amounts of bismuth, zinc or nickel, according to the origin (Smith and Turner).

A very thorough and well illustrated account of the preparation and treatment of sterling silver has been given by Sperry.⁴

¹ "The Forms of Electrolytically Precipitated Metals," *Zeit. Elektrochem.*, Vol. 19, p. 161; "Silver Mirror," *Ann. Chem.*, Vol. 387, p. 86; "Capillary Silver," *Ann. Chem.*, Vol. 390, p. 340; "Silver Separated from Stable Compounds," *Ann. Chem.*, Vol. 398, p. 1.

² HELDERMAN, *Journ. Inst. Metals*, 1916, No. 2, p. 84.

³ PETRENKO, *Zeit. anorg. Chem.*, 1906, Vol. 50, p. 136.

⁴ *Journ. Frank. Inst.*, Vol. 163, p. 109.

The metal described contained 925 parts of silver, 70 parts of copper and 5 parts of cadmium, the latter being added as a deoxidizer.

Tin.—Tin is highly malleable but somewhat less ductile, as its strength is low—about 4,600 lbs. It attains its maximum malleability at 100°C. but becomes brittle at about 200°C. Mechanical work and most impurities increase the tensile strength of tin. At low temperatures, tin changes into a gray, friable powder with a specific gravity of 5.8 as compared to 7.30 for ordinary white tin.¹ This peculiar disintegration has been studied principally by Professor Cohen and collaborators, who showed it to be due to an allotropic transformation of white tin into gray tin. The equilibrium temperature was located at 20°C. but the maximum rate of transformation was found to lie at -48°C.² This transformation is all the more dangerous because, once it starts, it can proceed even at ordinary temperatures and is called the “tin pest” on that account. At all times, except for a period during summer, ordinary tin is in the metastable condition and is therefore liable to such disintegration.

Another transformation exists in tin at about 200°C.³ or, more exactly, at 202.8°C.⁴ Above 200°, tin crystallizes in the rhombic system and is brittle, while below 200° tin crystallizes in the tetragonal system and is ductile. When bent, tin emits a “cry” which has been explained by Garland⁵ as being due to the breaking up of the crystals along their cleavage planes, although no crevices can be detected in slightly bent tin. Tin is sometimes called a “self annealing” metal on that account.

Analyses of Banca, Straits, and other grades of tin, have been given by Cowan.⁶ Banca tin contains about 99.96 per cent. tin and small amounts of arsenic, antimony, copper and iron. Straits tin contains about 99.80 per cent. tin and small amounts of lead, arsenic, antimony, copper, bismuth, and iron. Common

¹ This was first observed by ERDMAN in 1851 in some organ pipes, and later by FRITZSCHE in 1869.

² See *Zeit. phys. Chem.*, 1899, Vol. 30, p. 601; 1900, Vol. 33, p. 57; 1900, Vol. 35, p. 588.

³ TAMMANN, *Ann. der Phys.*, 1903, Vol. 10, p. 147.

⁴ SMITS and DE LEUW, *J. Chem. Soc.*, Vol. 104, 2, p. 141.

⁵ Cairo Scient. Soc., 1914, Vol. 8, p. 27.

⁶ *Trans. Amer. Inst. Met.*, 1914, Vol. 8, p. 196.

tin should contain 99 per cent. tin and refined tin at least 99.75 per cent. tin.

Tungsten.—Tungsten is produced at times as a compact granular metal and at times as a gray powder, according to its use. It is very hard and has a high specific gravity. There is little agreement as to the melting point but it probably lies above 3,200°C., while the boiling or volatilization point is about 3,700°C.

The uses of tungsten and ferro-tungsten have been given by Venator¹ as follows: as an ingredient in steel and high speed steel, in alloys, for metal filament lamps, in jewelry, dental metallurgy, etc. Tungsten can now be produced in such form that it can be drawn through diamond dies in the form of wire, in which form it is used as lamp filaments.² Other uses of ductile tungsten are as contacts, for the heating element of electric furnaces, as gauze, as targets for Roentgen tubes, in the tungsten-molybdenum thermocouple, for standard weights, and in standard c.m.f. cells.³ In Table 8 are given the properties of ductile tungsten as given by Fink.⁴

TABLE 8.—PROPERTIES OF DUCTILE TUNGSTEN

Density, 19.3 to 21.4.

Tensile strength, as wire, 450,000 to 600,000 lbs. per sq. in.

Young's Modulus, 60,000,000 lbs. per sq. in.

Reduction of Area—wire (diam. = 1.14 mils)—65 per cent.

Thermal Conductivity, 0.35 gm. cal. per cm. per sec. per 1°C. (Pt = 0.166) calculated—See Coolidge, *Trans. Amer. Inst. Elec. Eng.*, —, Vol. 31, p. 870.

Expansion coefficient, 4.3×10^{-6} , (Pt = 8.8×10^{-6}).

Specific heat, 0.0358 (Weiss).

Resistivity, at 25°C., Hard = 6.2 microhms per cm. cu.; Annealed = 5.0 microhms per cm. cu.

Temperature coefficient, 0° – 170° C. = 0.0051.

Hardness, 4.5 to 8.0 on the Mohs scale.

Chemical behavior, Insoluble in HCl, H₂SO₄, HNO₃, HF, NaOH, KOH (aq), K₂Cr₂O₇ + H₂SO₄. Soluble in mixtures of HF and HNO₃ and in fused nitrites and nitrates and peroxides.

According to Ruff, tungsten, in order to be ductile, must be free from oxide, iron and nickel, and practically free from sulphur,

¹ *Stahl u. Eisen*, 1908, Vol. 28, p. 255.

² See FINK, *Met. Chem. Eng.*, 1910, Vol. 8, p. 340, and MOORE, *Ibid.*, 1914, Vol. 12, p. 186.

³ See FINK, *Met. Chem. Eng.*, 1912, Vol. 10, pp. 580, 684.

⁴ *Journ. Ind. and Eng. Chem.*, 1913, Vol. 5, p. 9.

phosphorus and other non-metallic impurities, with less than 0.1 per cent. carbon.¹

One of the best treatises on tungsten, its preparation and uses, is "Die Metallurgie des Wolframs" (1911) by Mennicke and should be consulted for details. Two other very excellent articles are those of Ruff on the production of ductile tungsten² and "The Metallography of Tungsten" by Jeffries.³ In the latter paper, Doctor Jeffries advances a very interesting theory to explain the peculiar properties and behavior of ductile (fibrous) tungsten.

Zinc.—Zinc crystallizes in the octagonal system, rhombohedral form, and in the isometric system. Zinc ranks in malleability between lead and iron and in ductility, between copper and tin. In damp air it becomes coated with a basic carbonate which protects it from further corrosion. Zinc is electropositive to all other common metals, except magnesium, and precipitates all the ductile metals from solution except magnesium, iron and nickel. Pure zinc is almost unaffected by acids except nitric acid.

Allotropy.—The allotropy of zinc is somewhat in doubt on account of the influence of impurities. Benedicks, having in mind the change in rolling properties with temperature, measured the electrical resistance of zinc at different temperatures and located a transformation point at 170° and another point at 340°C.—the Le Chatelier point (1890). The point at 340°C. was verified by Lastschenko who located an anomaly at 340–350°C. by calorimetric determinations. Later this view was changed, as Benedicks and Arpi considered the points to be due to the presence of cadmium, which is hard to remove from zinc. Distilled zinc was said to exhibit no allotropic transformations.⁴ Cohen and Helder mann, who had done considerable work on the allotropy of zinc, still held to the idea that zinc has an allotropic transformation point at about 170°C. and considered the method used by Benedicks and Arpi to be at fault.⁵ The micrographic examinations of Petrenko indicate a recrystallization in zinc at some temperature around 300°C.⁶

¹ *Zeit. angewandte Chem.*, 1912, Vol. 25, p. 1889.

² *Loc. cit.*

³ *Bull. Amer. Inst. Min. Eng.*, June, 1918, p. 1037.

⁴ *Zeit. anorg. Chem.*, Vol. 88, p. 237.

⁵ *Verslag. Akad. Wet.*, Vol. 23, p. 546.

⁶ *Journ. Soc. Chem. Ind.*, 1914, Vol. 33, p. 1212.

This work failed to locate an allotropic transformation which might explain the rapid increase in malleability of zinc at temperatures above 100°C.; but this change in properties may be readily explained with the assistance of Jeffries' conceptions of the phenomena of working and annealing.¹ Thus rolling zinc sheets at temperatures above 100°C. is in reality "hot work" and results in a marked grain refinement.

Zinc, either cast or rolled, has a low elastic limit and no well-defined yield point and is relatively plastic. The tensile strength of thin rolled plate is about 24,000 pounds but this figure can be increased to 35,000 pounds or even 40,000 pounds by cold working. The elongation appears to vary considerably (with the composition and physical condition) but may be said to be over 20 per cent. for sheets which are rolled soft. Both the tensile strength and elongation may be materially lowered by annealing. The modulus of elasticity is about 11,500,000 pounds per square inch. The stress in shear is about 40 per cent. of that of mild steel.²

The four grades of commercial zinc, according to the American Society for Testing Materials, are given in Table 9.

TABLE 9.—SPECIFICATIONS FOR COMMERCIAL ZINC

	Pb Per Cent.	Fe Per Cent.	Cd Per Cent.	Pb + Fe + Cd Per Cent.
1. High grade, not over.....	0.07	0.03	0.05	0.10
2. Intermediate, not over.....	0.20	0.03	0.50	0.50
3. Brass special, not over.....	0.75	0.04	0.75	1.20
4. Prime western, not over.....	1.50	0.08		

Aluminum must be absent in all grades.

Effect of Impurities.—Lead is found in most makes of spelter, and in some up to 2 or 3 per cent. A moderate percentage increases the ductility and malleability without making it too tender. The presence of a small amount of lead in rolled sheet zinc may result in an increase in the hardness by its effect in raising the annealing temperature. Lead is especially undesirable in spelter which is to be used for high grade brass, but a moderate percentage is quite acceptable in ordinary brass.

According to Meyer, who determined the effect of ordinary

¹ This has been shown MATHEWSON, TREWIN and FINKELDY in a paper which should be referred to for the properties and behavior of zinc. *Bull. Amer. Inst. Min. Met. Eng.*, 1919, No. 153, p. 2775.

² See MOORE and TALBOT, *Chem. Eng.*, Vol. 15, p. 45.

impurities on zinc,¹ cadmium up to 0.2 per cent. improves the properties of zinc, but there is no advantage in adding more than 0.4 per cent. The effect of lead is particularly harmful when cadmium is also present.

Iron, up to 0.125 per cent. is not injurious but more iron reduces the malleability very seriously and makes zinc difficult to roll properly. ZnO also makes zinc difficult to work while copper, tin, and arsenic render zinc hard and brittle.²

One important point here is that the presence of a small amount of impurities makes it possible to produce zinc with a certain amount of "temper." The annealing temperature of pure zinc is so close to room temperature that rolling fails to increase its hardness. (Mathewson, Trewin and Finkeldy.)

Uses of Zinc.—Zinc is malleable at temperatures between 100° and 200°C. and is, accordingly, rolled into sheets which are used for various commercial purposes, particularly where resistance to corrosion is a factor. A metallographic study of the rolling and annealing of zinc has been made by Timoteef³ but, as yet, there is no well developed theory of the properties, working and microstructure of zinc. Tests by Hauser⁴ on the tensile properties of pure zinc failed to show any loss in strength or gain in ductility at 150°C. to explain the rolling properties of zinc. This point is also corroborated by the work of Haines who likewise found no anomaly in pure zinc around 100°C.⁵ Commercial zinc containing 0.52 per cent. lead became perceptibly harder at about 110°C. above which point it again became softer. Zinc is also used in making alloys, principally brass.

There has been an attempt made in recent years to improve the properties of zinc in order that it might be more extensively utilized in technical practice, which has been particularly true in Germany. It has been shown by Schulz that mechanical working benefits zinc while its hardness and toughness are increased by the addition of about 6 per cent. copper and 3 per cent. aluminum.

¹ *Metallurgie*, 1906, Vol. 3, p. 53.

² For the effects of impurities on zinc, see also ARNEMANN, *Metallurgie*, 1910, Vol. 7, p. 201, and FREEMAN, *Eng. and Min. Journ.*, 1915, Vol. 99, p. 990.

³ *Compt. Rend.*, 1912, Vol. 155, p. 430.

⁴ *Verh. Deut. Phys. Gesell.*, 1913, Vol. 15, 24, p. 1278.

⁵ *Proc. Roy. Soc., London*, 1911, A. Vol. 85, p. 526.

CHAPTER II

WHITE METAL ALLOYS—BEARING METALS

The alloys to be considered here are principally those of lead, tin, antimony, and zinc, to which other metals, such as copper, may be added to secure certain properties. These alloys find application in the arts on account of their low melting points and the ease with which they can be cast into shape, and certain useful technical properties which they possess.

Lead-Tin.—The lead-tin alloys were supposed originally to conform to a simple type of constitution diagram, similar to Type II *a*. More intensive investigations, however, have shown that lead is capable of dissolving tin in solid solution at higher temperatures, and that this tin is thrown out of solution, on

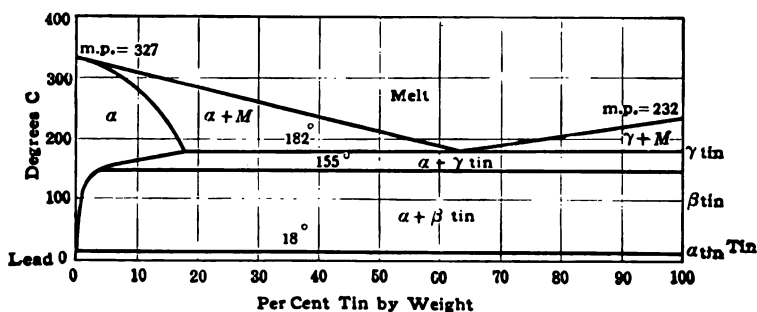


FIG. 17.—The lead-tin constitution diagram.

cooling, as a segregate. The diagram, as given by Guertler, is shown in Fig. 17. The eutectic point has been accurately determined by a number of observers and the values obtained by Rosenhain and Tucker¹ of 63 per cent. tin and 182°C. are used in the diagram. The solidus on the tin side is drawn to show practically complete insolubility of lead in solid tin (Mazzotto). The solidus on the lead side is also drawn according to the findings of Mazzotto, who employed a special method for making the determinations. This curve shows the solid solubility of tin in lead already mentioned. The solubility here shown, corresponds to that found by Rosenhain and Tucker after six weeks annealing,

¹ *Proc. Roy. Soc.*, 1909, Series A, Vol. 81, p. 331.

while on ordinary rates of cooling it comes between about 6 per cent. and 12 per cent. tin.¹

The very appreciable solubility at the eutectic temperature and the practical insolubility at lower temperatures, combined possibly with an allotropic transformation in tin at 161°C., gives rise to a peculiar heat effect at 155°C. on cooling, which however is not reproduced on heating.² As explained by Mazzotto³ after an extended investigation, these transformation points have no real place in the constitution diagram but are due to supercooling of the lead-tin solid solution. The tin of the solid solution, instead of separating out continuously from the eutectic temperature down, first forms at a lower temperature and with such intensity that a marked heat effect occurs on the cooling curves. In the alloys containing the eutectic the heat effect occurs at a constant temperature but, in the solid solution, the heat effect occurs at gradually lower temperatures with decrease in the tin content of the solid solution. On heating, the dissolution of tin in lead is gradual and continuous and no heat effect is recorded on the heating curve.

The addition of either tin to lead or lead to tin increases the hardness of the pure metals.⁴ The hardness increases comparatively rapidly with the first additions of either lead or tin and reaches a maximum at about 50 per cent. tin. The hardness of the alloy with 7 per cent. tin is said to be about the same as that of pure tin. The presence of small amounts of lead in tin is not readily detected unless some special test is applied. Considerable commercial tin contains lead in quantity and has essentially the same properties as pure tin; thus, the alloy with 10 per cent. lead gives the characteristic tin "cry." In this latter respect, lead differs from zinc inasmuch as 1 per cent. of zinc destroys this characteristic in tin.

Uses of the Lead-Tin Alloys.—The principal commercial uses of the lead-tin alloys are for solder, for the manufacture of various

¹ The eutectic point was given as 181°C. and 24.4 atomic per cent. Pb; the limits of solid solubility as 0.21 and 88 atomic per cent. Pb and the heat effect on cooling at 146°C., by DEGENS, *Zeit. anorg. Chem.*, 1909, Vol. 63, p. 207.

² This point has been considered in detail by GUERTLER, *Metallographie*, pp. 727 *et seq.*

³ *Int. Journ. Metallog.*, 1911, Vol. 2, p. 289.

⁴ See SAPOZHNIKOV, *Journ. Russ. Phys. Chem. Soc.*, Vol. 40, p. 91; STENQUIST, *Zeit. phys. Chemie*, 1910, Vol. 70, p. 536.

utensils, in which form they are known as "pewter," for toys and cheap jewelry, and as tempering baths in the heat treatment of steel.

Soft Solder.—The percentage of tin in solder varies with the work which must be done. In the electrical industry, solder with 50 per cent., or under, of lead is used. In special cases, such as for soldering certain tin utensils, a pure grade of tin is used. Tinsmiths use an alloy containing 60 per cent. tin which is very nearly the eutectic and therefore very fusible. The "half and half" solder with 50 per cent. tin is also extensively used and has good mechanical properties and gives a smooth surface. This alloy is also used for electrical fixtures. Plumbers use a lead-rich alloy containing from 60 to 67 per cent. lead. According to Granfield,¹ whose investigations of plumbers' solder have been consulted, this range of composition should be adhered to because these alloys contain sufficient lead to adhere to lead sheath and have a sufficient range of solidification for "wiping" a joint and yet they remain molten at a low enough temperature so that fusion or dissolution of the sheath can be avoided. The admixture of lead sheath in solders should be avoided because the melting point may be made too high, and the antimony, usually found in cable sheath, produces defective joints. Aluminum and zinc are also harmful impurities in plumbers' solder.

Pewter.—Pewter is used largely for drinking cups, pitchers and vessels for measuring liquids and, on account of the lesser resistance of lead and the danger of lead poisoning, only those alloys containing primary tin and the eutectic mixture should be used. The alloys are particularly susceptible to corrosion by acetic acid or vinegar when they contain free lead. The acetic acid which forms in moist wood was the source of considerable trouble when wooden ducts were used for lead conduits (Granfield). On this account pewter commonly contains 80 per cent. tin and above.

The eutectic alloy has a brilliant surface and is used in the manufacture of cheap jewelry and brilliants while the lead-rich alloys are used in the manufacture of toy soldiers and the like. Lead with 3 per cent. tin has been used extensively for sheathing for underground work and is superior to pure lead for the purpose.

Lead-Zinc.—The lead-zinc constitution diagram, as given by Guertler, is reproduced in Fig. 18. According to this diagram,

¹ T. H. GRANFIELD, Engineer for the American Telephone and Telegraph Company, and Graduate Student in Metallography.

lead and zinc are not appreciably soluble in each other even in the molten state. The liquid miscibility increases gradually until, at about 940°C., the two metals are completely soluble. We know at once, therefore, that melts of these two metals separate into two liquid layers, so that the alloys would hardly be of technical importance.

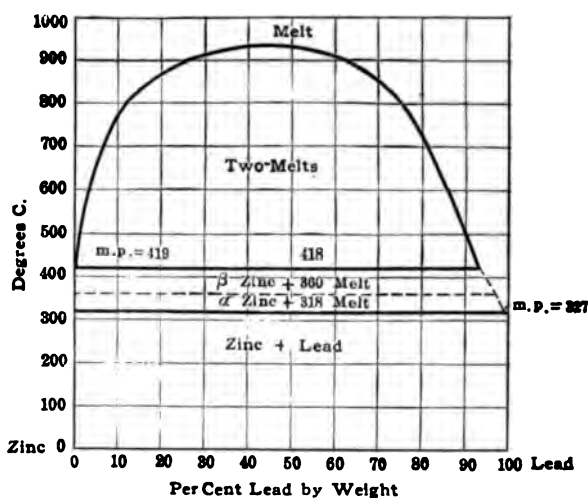


FIG. 18. --The lead-zinc constitution diagram.

This principle is utilized in the well-known Parke's process for the desilverization of lead bullion. Zinc is added to the lead bullion and immediately forms an alloy with the silver, containing crystals of Zn and Ag_2Zn_5 ¹ which is readily skimmed off and treated for silver.²

Lead-Antimony.—The lead-antimony diagram is given in Fig. 19. According to this diagram, lead and antimony are perfectly miscible in the liquid state but are practically insoluble in the solid state.³ No compounds are formed.⁴ The eutectic

¹ KREMAN and HOFFMEIER, *Monatsch. Chem.*, Vol. 32, p. 563.

² See also, BOGITCH, *Compt. Rend.*, 1914, Vol. 159, p. 178.

³ GONTERMANN, *Zeit. anorg. Chem.*, Vol. 55, p. 419.

⁴ In this connection, it should be pointed out that a heat effect was noted at 244.8°C. or just below the eutectic point (Gontermann). This has led GUERTLER to assume a compound of approximately the composition PbSb . The existence of such a compound seems to be substantiated by electrical conductivity measurements (Guertler) but not by thermoelectric force measurements (Rudolfi).

point is at 87.5 per cent. lead and 248°C. The alloys between lead and the eutectic point are composed of primary lead in dendritic formation with the eutectic as filling matter. The alloys on the other side of the eutectic contain primary antimony as cubical crystals. Unless the cooling is fairly rapid, the primary antimony crystals are forced upwards in the heavier lead-rich melt and form an antimony-rich upper layer, which can be seen as a bright crust. This behavior serves as a classical example of liquation or segregation during solidification.

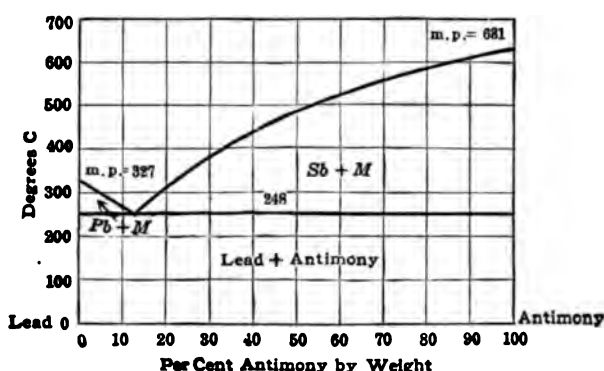


FIG. 19.—The lead-antimony constitution diagram.

The only alloys of commercial importance are those near the lead side and these are used on account of their plasticity, increased hardness and resistance to chemical corrosion as compared to lead and the ease with which they can be cast or rolled into shape. The hardness of lead is greatly affected by the first additions of antimony, as can be seen from Table 10.¹

TABLE 10.—HARDNESS OF LEAD-ANTIMONY ALLOYS

Per cent. antimony	Hardness in kg. per sq. mm.
0	4.31
4	8.00
8.28	12.05
13	17.7
17	13.25
20	15.9
40	18.75
74.35	21.2
100	39.8

Hardness numbers are for a pressure of 200 kg. (Brinell Test).

¹ SHAPOSHNIKOV and KANEVSKY, *Journ. Russ. Phys-Chem. Soc.*, 1908, Vol. 39, p. 901.

The maximum at 13 per cent. antimony coincides with the eutectic point and corresponds to the maximum in compressibility which was found by Charpy.¹

Uses of the Lead-Antimony Alloys.—Lead containing a small percentage of antimony is commonly called "hard lead" and is used in a variety of ways as a substitute for pure lead, for the reasons just stated. Lead sheath for conduits is an example, for which purpose a lead-antimony alloy has proven more reliable than the lead-tin alloy. A large amount of this alloy, containing about 10 per cent. antimony, was used during the recent war in the manufacture of shrapnel bullets. The alloy can be readily extruded and formed into shape and yet it is quite hard. Shot for guns and rifle bullets are made from antimonial lead. Lead with a few per cent. of antimony is used in the construction of storage batteries. Alloys containing larger amounts of antimony are used in the construction of pumps which must handle corrosive liquids. These alloys containing from 10 to 15 per cent. antimony have the following properties, according to the determinations of Professor Goodman (Law):

Elastic Limit, Tension, 1.00 to 0.92 tons per sq. in.; Compression, 1.00 tons per sq. in.

Maximum Stress, Tension, 3.20 to 2.90 tons per sq. in.; Compression, 7.50 tons per sq. in.

Young's Modulus, Tension, about 1700 tons per sq. in.; Compression, about 1800 tons per sq. in.

The elongation and reduction of area were both very low. No information is given regarding the method of preparing the alloys so that undoubtedly slightly different values could be readily obtained.²

Lead-Antimony alloys have also been used for type metal but, at present, ternary alloys with tin are preferred. These alloys will be considered later. The 67 lead: 33 antimony alloy is used for keys for musical instruments of the cheaper grades.

Antimony-Tin.—The antimony-tin constitution diagram, as given by Guertler, is reproduced in Fig. 20. The liquidus consists of four different branches corresponding to equilibria

¹ Contrib. a l'Etude des Alliages, p. 212.

² This is suggested by the work of SHAPOSHNIKOV and KANEVSKY, as they found (*loc. cit.*) a hardness number of 15.9 for the eutectic, in case the metal was poured in closed molds.

between four different solid phases and the melt.¹ According to electrical conductivity measurements, the compounds are Sn_3Sb_2 and SnSb .² Some confusion regarding the constitution of these alloys has been caused by retardation of the peritectic reactions and in general by the tardiness with which conditions of stable equilibrium are established. This gives rise to heat effects which apparently indicate an extension of the peritectic horizontals at 243°C . and 319°C . to above 60 per cent. antimony (Reinders and Williams). After sufficiently long annealing

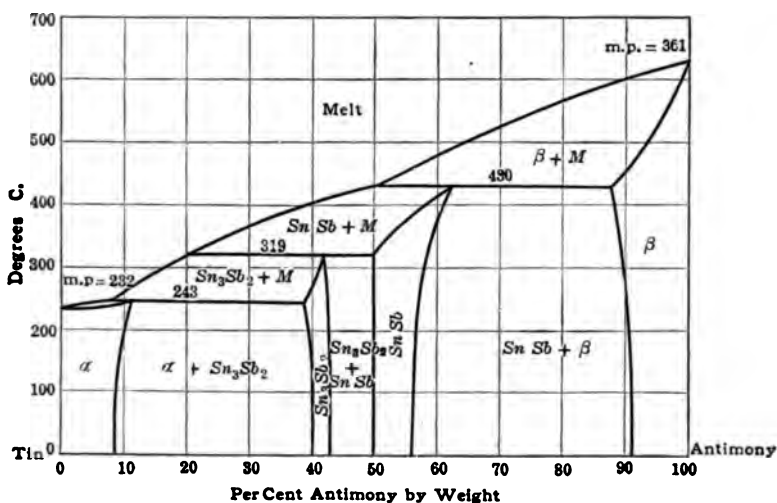


FIG. 20.—The tin-antimony constitution diagram.

these heat effects are found to disappear (Konstantinov and Smirnov). These alloys on the tin side, like the antimony-lead alloys, are subject to liquation. In this case the crystals of Sn_3Sb_2 are floated on top of the tin-rich melt.

Uses of the Tin-Antimony Alloys.—The principal use of the binary alloys of tin and antimony is in the manufacture of household and other utensils, in which case they are known as Britannia metal. These alloys usually contain about 5 to 10 per cent. antimony and a small amount of copper and zinc, the rest being

¹ REINDERS, *Proc. Inst. Mech. Eng.*, 1904, p. 209. Appendix III to 6th Report to Alloys Research Committee. Also, *Zeit. anorg. Chem.*, 1900, Vol. 25, p. 113. GALLAGHER, *Journ. Phys. Chem.*, 1906, Vol. 10, p. 93. WILLIAMS, *Zeit. anorg. Chem.*, 1907, Vol. 55, p. 1.

² KONSTANTINOV and SMIRNOV, *Intern. Journ. Metallography*, 1911-12, vol. 2, p. 152.

tin. Iron and zinc and an excess of antimony make Britannia metal brittle while copper, though increasing the ductility, lowers the fusibility and imparts a yellowish color. A small amount of lead is allowable, to increase the fusibility for casting purposes, but an excess gives a dull color.

Britannia metal can be easily rolled at room temperature and is not appreciably hardened thereby unless there is too much copper and antimony present. Heating to 100°C. materially softens the alloy and this treatment is used for stamping operations.¹ Britannia metal, in common with other metals of this type is hardened somewhat by quenching. Structurally, Britannia metal probably consists of small hard crystals of Cu_3Sn in the tin-antimony solid solution. The Cu_3Sn crystals appear white on a black background when etching is done with one per cent. solution of nitric acid in alcohol.

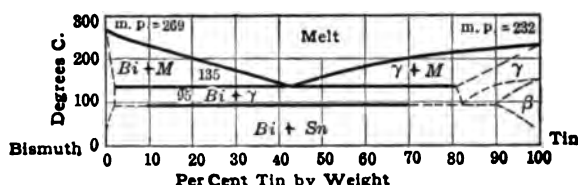


FIG. 21.—The bismuth-tin constitution diagram.

Certain of the tin-rich alloys, containing hard crystals of Sn_3Sb_2 embedded in the tin-rich matrix, have been used as bearing metals but the ternary alloys, to be considered later, are more satisfactory.

Tin-Zinc.—The constitution diagram of the tin-zinc alloys is simple, inasmuch as tin and zinc are soluble in all proportions in the liquid state and insoluble in the solid state. A eutectic point comes at about 92 per cent. tin and 197°C. These alloys apparently find no industrial application. The alloy with 75 per cent. tin is said to flow freely on casting and to produce sharp castings, due to slight expansion on solidifying, so that it can be used for metal patterns (Thurston).

Bismuth-Tin.—The bismuth-tin constitution diagram is reproduced in Fig. 21 as given by Guertler. The eutectic comes at about 42 per cent. tin and melts at 135°C., or only slightly above the boiling point of water. The addition of other metals

¹ For an excellent treatise on Britannia metal, see THOMPSON and ORME. *Journ. Inst. Met.*, 1919, No. 2, p. 203.

still further lowers the melting point and produces the "fusible" alloys, melting at temperatures under 100°C. As shown on the diagram, the tin-rich solid solution breaks down at 95°C. into a eutectoid composed of nearly pure bismuth and nearly pure tin. The pure binary alloys of bismuth and tin have no commercial application at present.

Antimony-Zinc.—The antimony-zinc constitution diagram, as given by Guertler, is reproduced in Fig. 22.¹ Antimony and zinc are soluble in all proportions in the liquid state but are practically insoluble in the solid state, although two intermetallic compounds are known to form. The liquidus passes through

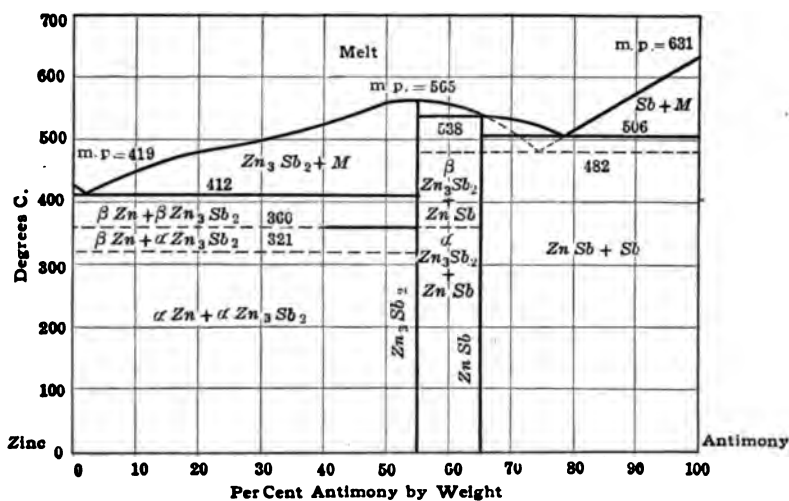


FIG. 22.—The antimony-zinc constitution diagram.

a maximum at 55 per cent. antimony which corresponds to the compound Sb_2Zn_3 . At 65.8 per cent. Sb, the liquidus passes through a transition point which corresponds to the formation of the compound $SbSn$. This compound has an exceedingly low nuclei number at these temperatures, so that, under ordinary conditions of cooling, only Sb_2Zn_3 forms and solidification proceeds according to the dotted lines. The metastable eutectic solidifies at 482°C. At temperatures in the neighborhood of 400°C. reversion to the stable state occurs spontaneously with

¹ MÖNKMEYER, *Zeit. anorg. Chem.*, 1905, Vol. 43, p. 182; SCHEMITSCHUSCHNY, *Zeit. anorg. Chem.*, 1906, Vol. 49, p. 384. CURRY, *Journ. Phys. Chem.*, 1909, Vol. 13, p. 589. ARNEMANN, *Metallurgie*, 1910, Vol. 7, p. 201.

the generation of considerable heat (recalescence). If the melt is inoculated with the stable phase, SbSn, solidification proceeds according to the solid lines and the SnSb-Sb eutectic solidifies at 506°C.¹

The transformations which occur in the solid alloys toward the zinc end of this series are rather complex and not as yet explained entirely satisfactorily. In the diagram, the compound Sb_2Zn_3 is shown to be allotropic with a transformation point at 360°C. Furthermore, the range of composition of the phase is practically limited to the one single composition. Curry, on the other hand, makes entirely different assumptions regarding the nature of these alloys. He holds that the compound Sb_2Zn_3 , as such, does not exist but that the phase is simply an intermediary solid solution, one which, however, occurs in three different modifications, α , β , and γ . A range of composition of several per cent. is assigned to these phases and the transformation temperatures are assumed to vary very markedly with change of composition over this range. These three modifications are brought out only by means of heating curves, both microscopic examination and cooling curves failing in this respect.

Lead-Bismuth.—The constitution diagram, as given by Güertler, is shown in Fig. 23. From this diagram we see that the eutectic alloy solidifies at 125°C. which is even lower than the freezing point of the bismuth-tin eutectic. The solubility of bismuth in lead, as determined by careful thermal analysis over the entire range from pure lead to the eutectic, is considerable, as is shown.²

The best decision as to the solubility at room temperature seems to be as represented, particularly as an accurate method of thermal analysis fails to give any heat effect in the solid state, as in the case of the lead-tin alloys.³ Evidence indicating practically complete segregation or elimination of the bismuth from the solution is found in the work of Puschin, according to which the alloys rich in lead show the same potential as pure lead.⁴

Evidence bearing on the solubility of lead in bismuth is quite

¹ We have a parallel case in the alloys of cadmium and zinc, in which case the compound Cd_3Sb_2 forms from the melt, only to break down in a few moments into the compound CdSb .

² See for example, MAZZOTTO.

³ MAZZOTTO, *Int. Journ. Metall.*, 1913, Vol. 4, p. 273.

⁴ *Journ. Russ. Chem. Soc.*, 1908, Vol. 39, p. 869.

conclusive that a small amount, as shown by the diagram, is dissolved at the eutectic temperature and that no appreciable lead segregation occurs on cooling to room temperature. This is borne out by electrolytic potential determinations,¹ and electrical conductivity determinations.²

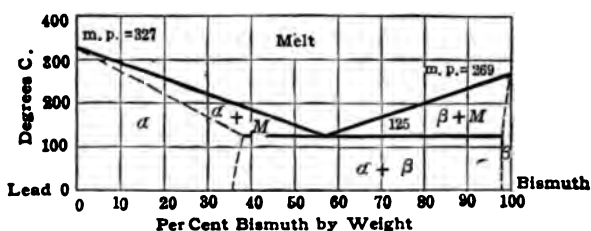


FIG. 23.—The lead-bismuth constitution diagram.

The alloys, aside from their use in fusible alloys, do not appear to have a commercial application. They appear to have been studied largely on account of their scientific interest.

Lead-Cadmium.—The alloys of lead and cadmium have not been investigated metallographically with the same care which has been accorded the other alloys of this class, which have al-

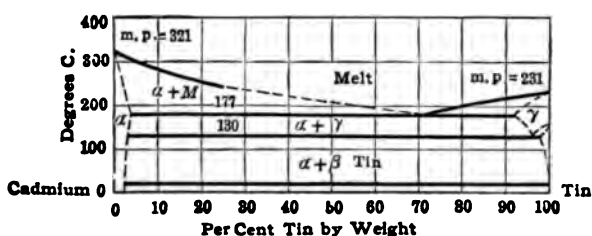


FIG. 24.—The cadmium-tin constitution diagram.

ready been considered. The eutectic solidification point is given as 249°C. (Stoffel). Lead, in all probability dissolves a small amount of cadmium in solid solution (Guertler).

Cadmium-Tin.—The constitution diagram of the cadmium-tin alloys is given in Fig. 24 which is essentially the same as that given by Schleicher.³ According to this diagram the eutectic solidifies at 177°C. which is appreciably higher than those of the

¹ PUSCHIN, *Loc. cit.*

² SCHULTEE, *Drudes Ann.*, 1902, Vol. 314, p. 555. See SCHENCK, *Physik. Zeit.*, 1907, Vol. 8, p. 239. See also, HEROLD, *Zeit. anorg. Chem.*, 1920, Vol. 112, p. 131.

³ *Intern. Journ. Metallography*, 1911-12, Vol. 2, p. 76.

bismuth-tin or lead-bismuth alloys. The high temperature modification of tin, or γ tin, dissolves up to nearly 10 per cent. cadmium in solid solution. Through a eutectoid inversion, nearly all of this cadmium is thrown out of solution when the γ tin changes into β tin. These conclusions are verified by the careful work of Mazzotto, who employed his accurate method of thermal analysis to check the points.¹ According to measurements of electrical conductivity and thermoelectric force, the reciprocal solubilities of cadmium and tin are 3 per cent. each.²

Bismuth-Cadmium.—Bismuth and cadmium form a very simple series of alloys. They are soluble in all proportions in the liquid state,³ and practically insoluble in the solid state,¹ while the eutectic alloy contains 40 per cent. cadmium and solidifies at 140°C. The constitution diagram has been determined by a number of investigators and is now known with great accuracy.⁴

Bismuth-Copper.—The copper-bismuth constitution diagram, as given by Guertler, is reproduced in Fig. 25. The data on which this diagram is largely based are taken from the work of Portevin⁵ and Jeriomin.⁶ The eutectic point is practically pure bismuth but is taken as 0.25 per cent. copper, while the reciprocal solubility of bismuth and copper is at the most but a few tenths of a per cent. The influence of bismuth on copper is of considerable technical importance and has been considerably discussed in the literature. According to Laurie,⁷ the allowable limit of bismuth in copper to be rolled, either hot or cold, is 0.005

¹ *Trans. Amer. Metallurgical Inst.*, 1913, Vol. 4, p. 13. See also an additional contribution in 1913. *Trans. Amer. Inst.*, 1913, Vol. 4, p. 194.

² *Revue Sci. Instrum. et Chim.*, 1915, Vol. 98, p. 97.

³ Thermoelectric force measurements indicate a slight solubility of Cd in Bi. See *Revue Sci. Instrum. et Chim.*, 1913, Vol. 87, p. 80. Earlier determinations by Berthel (1880) indicate an appreciable reciprocal solubility of these metals but his results, like many other results obtained by physical measurements, cannot be interpreted with the same confidence accorded them by the more exact thermodynamic methods.

⁴ *Trans. Amer. Metallurgical Inst.*, 1907, Vol. 35, p. 148; *Portevin, Rev.*

⁵ *Ann. Chim. Phys.*, 1907, Vol. 10, p. 100; *Portevin, Rev. Metall.*, 1914, Vol. 11, p. 100; *Portevin, Rev. Metall.*, 1914, Vol. 11, p. 100.

⁶ *Ann. Chim. Phys.*, 1907, Vol. 10, p. 100.

⁷ *Ann. Chim. Phys.*, 1907, Vol. 10, p. 100.

per cent., while 0.02 per cent. makes copper cold-short and 0.05 per cent. makes copper red-short.

Antimony-Copper.—The antimony-copper constitution diagram has been determined by Carpenter.¹ The principal difference between this determination and the earlier one by Baikoff,² for our present purposes, is in the amount of antimony which can be dissolved by copper. Ordinarily, antimony is supposed to be soluble to a very limited extent, 0.3 per cent. More recent observations, both of the melting points and

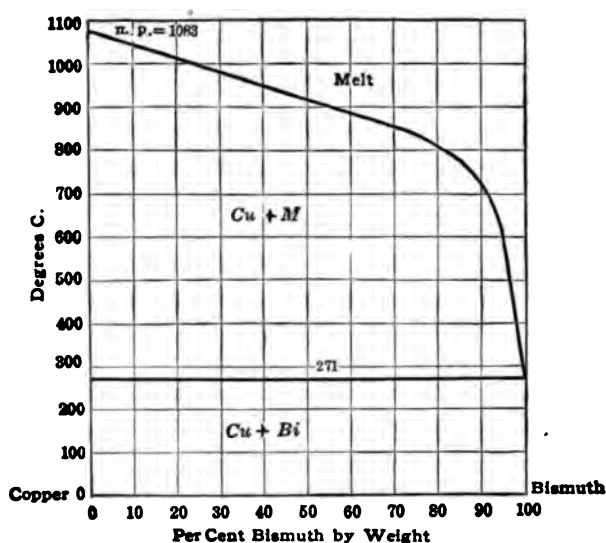


FIG. 25.—The copper-bismuth constitution diagram.

physical properties, have shown that Cu_3Sb does not exist as an individual compound (phase) and that it should be regarded as a solid solution.

Ternary and Other Alloys.—Under this heading will be considered certain ternary and quaternary white metal alloys, arranged according to their industrial application.

The Bearing Metal Alloys.—Without attempting a detailed discussion, it may be said that bearing metals are selected with regard for the following points.³ A bearing, first of all, must be

¹ *Intern. Journ. Metallography*, 1913, Vol. 4, p. 300.

² *Journ. Russ. Phys. Chem. Soc.*, 1904, Vol. 36, p. 111.

³ *References:* CHARPY, *Contrib. à l'Etude des Alliages*. HIORNS, *Eng. Mag.*, 1908, Vol. 36, p. 1023; a lecture before the Birmingham Assoc. of Mech.

able to resist wear, which is best secured by having present a constituent, or constituents, which are relatively hard. In this way any tendency to abraid or "cut" the bearing is resisted and most of the direct pressure is taken up by the hard constituent. It is also known by experiment that the frictional resistance offered by metals or alloys decreases as the hardness increases and, furthermore, that the load required to produce "gripping" is likewise greater for the hard alloys. For these reasons it is essential for a good bearing metal to have a certain amount of a hard metal or alloy, the exact amount depending on the service required.

The second requirement of a bearing metal is that it must have a certain amount of plasticity or "give" in order to conform to the shaft and thus distribute the load uniformly. Otherwise the load, due to lack of perfect adjustment, would be concentrated at points, with the result that the bearing would run hot, from undue friction, and "cut." This requirement is met by having a softer and more pliable constituent, one which is capable of deforming somewhat under the load.

From this it is apparent that bearing metals must be composed of a hard part and a pliable part. The pliable, or soft, part wears away more rapidly than the hard part so that the actual bearing surfaces are supplied by the hard part, which is usually present as small crystals uniformly distributed throughout the bearing. As these particles finally wear away, others are exposed to take up the load and so the bearing surfaces are continually replenished.

A third and very obvious requirement is that the bearing, as a whole, must be strong enough to resist the pressures applied, otherwise the bearing would be immediately forced out from under the load. This requirement determines, to a large extent, the actual metals to be used in the manufacture of the bearing, and their relative amounts.

The low coefficient of friction (of the hard constituent) is actually of minor consequence because the surfaces are kept well oiled and the friction depends upon the oil used, rather than upon the metals. In case of faulty lubrication, the low coefficient of friction and hardness of the hard constituent are of material, if only temporary, benefit.

Eng. reprinted in the *Mechanical Engineer*, Dec. 25, 1908; *Mechanical Engineers Handbook*, article by G. H. CLAMER; *Literature of the Ajax Metal Company*, Philadelphia.

Bearing metals may be conveniently classified, according to the principal metal constituent, as copper-base, tin-base, lead-base and zinc-base bearing metals, which classification will be followed here.

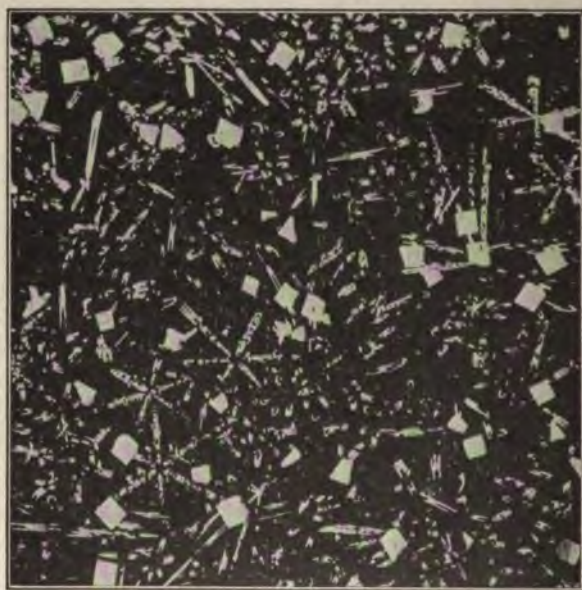
Copper-Base Bearing Metals.—The copper-base bearing metals are the strongest of the bearing metals which are in general use and are used in case exceptionally heavy pressures or severe pounding is encountered. Originally these alloys were simply binary alloys of copper and tin but as made at present, they contain lead as well. This lead makes the bearing more plastic and better able to yield to local excessive pressure. These alloys will receive a fuller account under "bronze."

Tin-Base Bearing Metals.—In this class are the Babbitt metals, so named after the inventor, Isaac Babbitt, who first employed the soft alloys as bearing metals. The commonest alloys of this type are the tin-antimony-copper alloys. There are two grades, known respectively as Soft Genuine Babbitt and Hard Genuine Babbitt. In the former the composition varies between 88 and 91 per cent. tin, 4 to $4\frac{1}{2}$ per cent. copper and $4\frac{1}{2}$ to 8 per cent. antimony. The S.A.E. specification is tin, 89 per cent. ± 2 per cent.; antimony, 7 per cent. ± 1 per cent.; and copper 4 per cent. ± 1 per cent. Impurities should be low or present only in traces. Die-cast bearings are also made from these compositions. The composition of the latter varies between 80 and 83 per cent. tin, and $8\frac{1}{2}$ to 10 per cent. of copper and antimony. The S.A.E. specification is tin 84 per cent. ± 2 per cent., antimony 9 per cent. ± 1 per cent., and copper 7 per cent. ± 1 per cent.

In these alloys copper and antimony are the hardening elements, the former by forming Cu_3Sn (see "bronze") which occurs as needles or star-shaped crystallites, and the latter by forming SnSb which occurs as cubes. The casting of these alloys is a very important step and the rate of cooling should be such that the SnSb crystals measure about 0.25 mm. across (Behrens and Baucke). The pouring temperature has been given as about 430°C . (810°F .) and the metal should be cast about a chill which has previously been heated to about 100°C . (212°F .) (Clamer).¹

¹ The babbitt metal should be just hot enough so that a soft pine stick (match) smokes the instant it is inserted in the molten metal. For the effect of pouring temperature, rate of cooling, chilling, etc. see FRY and ROSENHAIN, *Journ. Inst. Met.*, 1919, No. 2, p. 217. FRY and ROSENHAIN noted that hammering or dressing the surface shatters the hard crystals and they doubted the value of such a treatment.

According to the work of Charpy, the useful alloys of tin, antimony and copper, lie to the tin side of the line on the ternary diagram running from 15 per cent. copper to 25 per cent. antimony. The compressive strength, taken as the load required to compress a cylinder 15 mm. in height and 10 sq. mm. cross sectional area by 0.2 mm., increases with the copper and antimony content from about 500 kg. to nearly 1500 kg. The structure of a bearing metal typical of this group is reproduced in Fig. 26.



× 50

FIG. 26.—Bearing metal. Cast at 400°C. in warm sand. Composition: Tin, 86.84 per cent.; Antimony, 8.76 per cent.; Copper, 4.4 per cent. Brinell number 26. (*Fry and Rosenhain.*)

These bearing metals are used in high grade machinery where an exceptionally fine bearing is required and where the loads are heavy and severe pounding is apt to occur. The proportions of copper and antimony are regulated to the requirements of the service.

Lead is at times added to the tin-copper-antimony alloys and in general produces a softer alloy and one which is more apt to flow under heavy pressure. According to the work of Smith and Humphries, who added lead to a standard alloy with 83

per cent. tin, 11 per cent. antimony and 6 per cent. copper, the addition of lead results in an improvement¹ although the tin content should always be above 50 per cent., the antimony not under 12 per cent. and the copper not under 3 per cent. (Clamer). Small amounts of lead added to soft Babbitt (Sn 90, Sb 8, Cu 2) are known to increase the Brinell hardness number and to render the Babbitt less sensitive to temperature. Tests conducted at

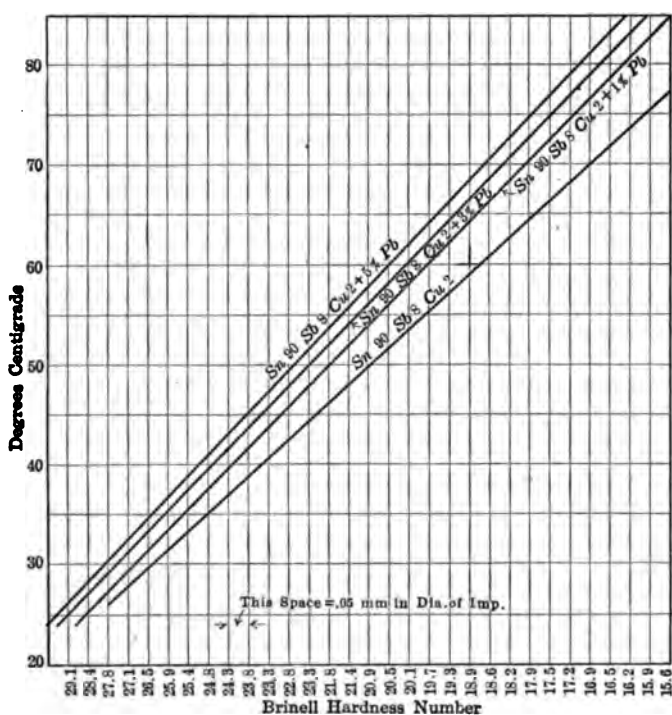


FIG. 27.—Effect of lead on hardness of A babbitt.

the Westinghouse Electric and Manufacturing Company bearing on this point are reproduced in Fig. 27.² The Babbitt with 84 per cent. tin, 10 per cent. antimony, 5 per cent. copper and 1 per cent. lead is given by Förg as representing the most satisfactory bearing metal for most purposes.³ If too much lead is added it forms a fusible lead-tin eutectic which is liable to melt and flow out of the bearing if the lubrication is defective.

¹ *Journ. Inst. Metals*, 1911, No. 1, p. 194.

² JONES, *Bull. Amer. Inst. Min. Eng.*, 1918, No. 140, p. 1395.

³ *Intern. Journ. Metallography*, 1916, Vol. 8, p. 68.

Tin-base bearing metals containing copper and zinc are also used, principally for marine bearings. The S.A.E. specifications for this alloy (Parson's White Brass) call for more than 65 per cent. tin, zinc 28 to 30 per cent. and copper 3 to 6 per cent. The alloy pours sluggishly and therefore can not be cast into thin sections. On account of the high casting temperature it is apt to be somewhat porous and should be peined to improve its properties. Increasing the copper content increases the strength but detracts somewhat from its wearing qualities. Its physical properties have been given as follows—tin 64 per cent., zinc 34 per cent., copper 2 per cent.—T.S., 12,500 lbs. per sq. in.; El. Lt., 8,000 lbs. per sq. in.; Elong. on 2 in., 20.5 per cent.; and Reduction of Area, 17.5 per cent.; melting point, 360°C.; pouring temperature, red heat (Clamer); and coefficient of friction, 0.0077.¹

Lead-Base Bearing Metals.—The lead-base bearing metals are those containing more than 50 per cent. of lead, or lead which has been hardened by antimony, sometimes with the addition of tin or tin and copper.

The constitution of the lead-antimony alloys has already been given. The compressive strength of the lead-antimony alloys increases as antimony is added up to the eutectic point at 13 per cent. antimony, beyond which point it increases very slowly with further addition of antimony (Charpy). The load required to produce a permanent deformation of 0.2 mm. in the standard test bar was 650 kg. as compared to 500 to 1500 kg. for Babbitt metal. This lack of compressive strength brings out the principal disadvantage of the use of lead-base bearing metals, *i.e.*, the ease with which they flow under pressure. However, if the service is such that there is no serious danger from this source, these alloys have excellent bearing qualities and are perhaps the most economical in use at present.

The alloy of lowest antimony content is the No. 4 Babbitt which contains from 10 to 12 per cent. antimony. More than 20 per cent. antimony makes the alloy too brittle for commercial use.

Lead-Tin-Antimony Bearing Metals.—The addition of tin to the lead-antimony alloys improves the properties of the matrix, or the lead-antimony eutectic and diminishes the hardness and brittleness of the hard crystals of antimony. The latter effect

¹ JONES, *Metal Industry*, May, 1905.

is probably due to the dissolution of the tin in the antimony to form the antimony-rich solid solution—see Fig. 20. The commercial alloys should contain more than 10 per cent. tin but not more than 20 per cent., and from 10 to 18 per cent. antimony (Charpy). The compressive strength determined by Charpy was found to be about 1764 pounds for a compression of 0.008 inch.

The constitution of the lead-tin-antimony alloys has been investigated by Campbell and Elder¹ and by Loebe.² More recently these alloys have been studied by Heyn and Bauer in their extensive investigation of the white metal and bearing metal alloys.³ This work has shown that the compositions generally employed for bearing metals consist of hard crystals of the SbSn-Sb solid solution in a matrix which is essentially the same as the eutectic of the lead-antimony series, there being no ternary eutectic. An increase in the relative amount of tin produces envelopes of the softer SbSn compound around the hard crystals of the solid solution. The following alloys studied by Campbell and Elbert and Loebe showed simply the hard cubical crystals of the SbSn-Sb solid solution: Pb 80, Sn 10, Sb 10; Pb 80, Sn 5, Sb 15; Pb 78, Sn 11, Sb 11; and Pb 65, Sn 10, Sb 25.

Copper is frequently added to these bearing metals as a hardening agent. The amount of copper which can be added depends upon the tin content, which is not over 0.5 per cent. for 10 per cent. tin and not over 1 per cent. for 20 per cent. tin (Clamer). Heyn and Bauer have noted that copper lessens the tendency of lead to liquefy in these alloys.

The use of the lead-base bearing metals has been particularly advocated since the scarcity of tin has become acute and it has developed from tests made at the Westinghouse Electric and Manufacturing Company that the lead-base alloy, at more elevated temperatures, is actually harder than the soft genuine Babbitt. The curves in Fig. 28 represent the variation in Brinell hardness of these bearing metals with rise in temperature.⁴ Results obtained with a hard genuine Babbitt are added for comparison although it was remarked that its hardness is

¹ *School of Mines Quarterly*, 1911, Vol. 32, p. 244.

² *Metallurgie*, 1911, Vol. 8, pp. 7, 33.

³ Ver. Bef. Gewerbfl., 1914, *Beiheft*, Mar. 30. See also, BAUER, *Stahl u. Eisen*, 1915, Vol. 35, p. 445 and p. 553.

⁴ JONES, *Bull. Amer. Inst. Min. Eng.*, 1918, No. 140, p. 1395.

normally about 38. The practical results obtained with the lead-base bearing metals have likewise shown its superiority and consequently it is now being used by that company to the exclusion of the soft tin-base Babbitt. Only when bearing pressures are unusually high is the hard genuine Babbitt -B- used.

Zinc-Base Bearing Metals.—The zinc-rich alloys possess many excellent characteristics which fit them for bearing metals, such

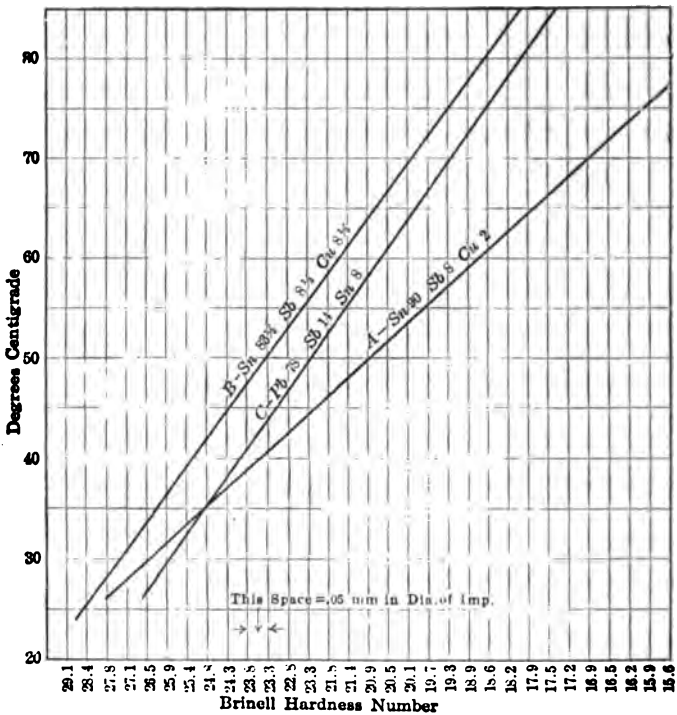


FIG. 28.—Hardness of three babbitts at varying temperatures.

as low coefficient of friction, low specific gravity, machinability, low price, and casting properties (Clamer). The principal disadvantage is the deterioration on heating (brittleness) and unless the bearing can be frequently inspected and maintained in correct adjustment, it is liable to grip the journal. On this account their use is limited although recommended for high speed bearings which are lightly loaded. Two common alloys are Lumen metal with 85 per cent. zinc, 10 per cent. copper and 5 per cent.

aluminum, and Fenton's alloy with 79 per cent. zinc, 16 per cent. tin and 5 per cent. copper.

Summary.—In general we may say, regarding the effects of various metals in bearing metals, that:

1. Friction is reduced by lead, the lead resembling graphite very much in this respect. Antimony also reduces the friction but not as much as lead.

2. Hardness is increased by antimony and copper.

3. Plasticity, and incidentally weakness under pressure, is increased by lead and to a lesser extent by tin. Tin is stronger than lead.

4. The melting point is lowered by lead and tin and is raised by copper and antimony.

5. Fluidity is increased by phosphorus and aluminum which act as fluxes.

6. Toughness is increased by tin and copper and is decreased by antimony.

Type Metal.—The principal requirement placed on type metal is that it must produce sharp castings on a small scale, for on that depends the quality of the work done. The other requirements are that it must be sufficiently resistant to the pressures used and that it must not be expensive. The compositions which are commonly used for this work are as follows (Clamer):

TABLE 11.—TYPE METAL COMPOSITIONS

Kind	Pb, per cent.	Sb, per cent.	Sn, per cent.	Cu, per cent.
Linotype metal.....	79	16	5	...
Monotype metal.....	76	16	8	...
Stereotype metal.....	83.75	11.75	4	0.5
Electrotype metal.....	92	4	4	...

Alloys containing more tin and antimony are said by Law to give better results for high-class work, but the cost is excessive for most purposes. Such a composition is said to be lead 50, tin 25, and antimony 25.

Other White Metal Alloys.—The white metal alloys are used for other purposes such as die-castings, slush metal castings, packing metal, fusible alloys,¹ etc.

¹ The lead-tin-bismuth alloys form the basis of the fusible alloys. The addition of cadmium still further lowers the melting point. The melting points of certain of these alloys are appended.

Alloy	Bi	Pb	Sn	Cd	Melting point	
					°C.	°F.
Rose's metal.....	50	28.1	24.6	110	230
Ternary eutectic.....	52	32	16	94	201
Wood's metal.....	50	25	12.5	12.5	68	154

The melting point can be still further lowered by the addition of mercury, even to 98°F. for anatomical purposes.

CHAPTER III

THE LIGHT METAL ALLOYS¹

It was noted in Chapter I that pure or commercial aluminum has sufficiently valuable properties to warrant its use on quite a large scale. The properties which make it of particular interest, considering now the commercial product which contains iron and silicon in amounts up to 0.50 per cent., are its low specific gravity of 2.70, its tensile strength of about 13,000 pounds per square inch in the cast or annealed state, its high ductility as shown by an elongation of 25 to 35 per cent. in the tensile test, its high conductivity of electricity (61, as compared to 100 for copper) and of heat (48, as compared to 100 for copper, or 0.50 K), and adequate resistance to corrosion under normal conditions. Combined with this are the abundance of aluminum in nature and the comparative ease with which it can be recovered in the electric furnace. The pure metal, however, has little use except in the worked condition as wire, tubing, sheets, etc.

In the alloyed condition, within certain limitations, advantage can again be taken of these valuable properties while the tensile strength can be increased and parts can be made in the forged and heat treated condition. It is due to these characteristics of the so-called "light metal alloys" that the alloys rich in aluminum have found their extended application, particularly in the automotive industries where lightness, strength, and durability are such important factors.

In the past there has been a great amount of research work done on aluminum alloys the results of which have been kept as carefully guarded secrets, except in so far as they might be of use in exploiting the alloys in question.² More reliable information is to be had from reports such as those of the Alloys Re-

¹ The Bureau of Standards has issued a *Circular* on Aluminum and its light metal alloys, 1919, No. 76, which contains a very thorough account of the metallography and properties of these alloys. This circular has been freely consulted in the preparation of this chapter.

² This question has been discussed by ANDERSON, *Paper* No. 14, of the Minerals Investigation Series of the U. S. Bureau of Mines, April, 1919.

search Committee of the Institution of Mechanical Engineers of Great Britain and of the U. S. Bureau of Standards. We have also had some valuable contributions from works laboratories, such as the Research Laboratory of the Aluminum Castings Company, whose interest lies, not in the exploiting of some particular alloy, but in developing materials and processes which can be used commercially in standard engineering practice. This latter kind of research is of particular value to engineers because of the great amount of attention paid to the production and use of the alloys.

The effect of adding a second metal to aluminum is to increase the tensile strength and lower the ductility. This is shown by Fig. 29 for copper, zinc, nickel and iron.¹ The specific gravity

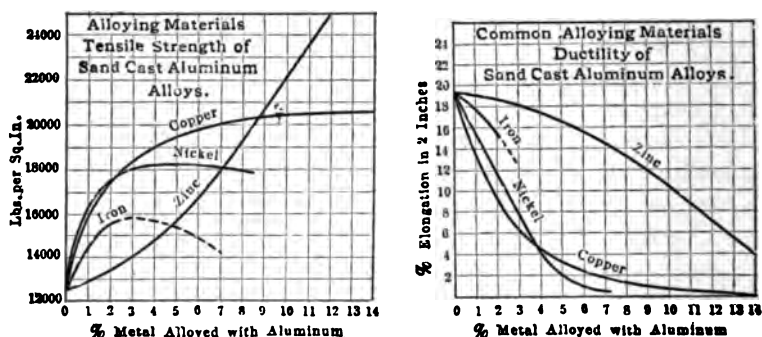


FIG. 29.—Tensile strength and elongation of sand cast aluminum alloys. (Rollason.)

is likewise increased but when it reaches about 3.0, which figure seems to hold irrespective of the added element, the ductility has dropped so low that further addition would not be worth while. For this reason only those alloys comparatively rich in aluminum need be considered here.

The Constitution of the Aluminum Alloys.—There is a very close relation between the physical characteristics of the light aluminum alloys and their constitution and microstructure and consequently the purely theoretical aspects have received considerable attention. The basis for this work is the information derived from the study of the constitution of the alloys and the structural relationships of the microconstituents. In the follow-

¹ ROLLASON, Alloyed Aluminum as an Engineering Material, *Advance Conv.*

ing we shall pass in brief review the aluminum ends of the important alloy systems. A very excellent treatise on the metallography of aluminum and its alloys is that of Hanson and Archbutt who describe methods for preparing microsections and of etching so as to distinguish between the various constituents which are most apt to be present.¹

Aluminum-Copper.—The complete constitution diagram and a more thorough discussion of the aluminum copper alloys will be given in the succeeding chapter. In Fig. 30 we have an enlarged

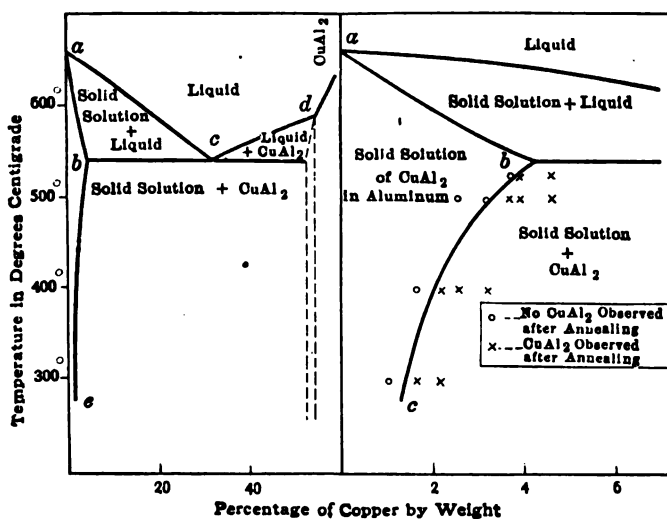


FIG. 30.—The aluminum end of the aluminum-copper diagram. (Merica, Waltenberg and Scott.)

view of the aluminum end of the series, as given by Merica. The eutectic of aluminum and CuAl₂ comes at 32 per cent. copper and 545 degrees Cent. The solubility of copper in aluminum at the eutectic temperature is about 4 per cent. but it decreases considerably as the temperature falls to room temperature. On slow cooling, the compound CuAl₂ separates out as a segregate but this action can be inhibited by quenching from 500 degrees Cent. This behavior forms the basis of the heat treat-

¹ HANSON and ARCHBUTT, *Journ. Inst. Met.*, 1919, No. 1, p. 291. The metallography of the aluminum alloys, principally those of copper and magnesium, have been considered by MERICA, WALTENBERG and FREEMAN. *Bull. Amer. Inst. Min. and Met. Eng.*, 1919, No. 151, p. 1031.

ment of alloys of this type and will be considered again under duralumin.

The structure of an alloy with 8 per cent. copper is shown in Fig. 31. The compound, which here occurs in the eutectic, forms a net work and outlines the crystallites or dendrites of the solid solution. This compound is brittle and serves to cut down the ductility so that these alloys are generally used in the cast condition for parts which require strength and rigidity but which do not require ductility and toughness. Hanson and Archbutt recommend etching with a 20 per cent. solution of nitric acid in water at 70 degrees Cent. The specimen is immersed for



FIG. 31.—Microstructure of an eight per cent. copper-aluminum alloy showing CuAl_2 . (Archer.)

a few seconds and then plunged immediately into cold water. CuAl_2 is colored dark brown by this treatment but most other constituents are unattacked.

The alloy represented by this photomicrograph is commonly used industrially. It contains 7.00 to 8.50 per cent. copper and not over 1.70 per cent. impurities. Its specific gravity is about 2.86 and when cast in green sand has an average tensile strength of 20,000 pounds per square inch and an elongation on two inches of 1.5 per cent. The amount of impurities permitted allows for the use of secondary metal and of cast iron crucibles for melting or even the intentional addition of other elements to increase the strength. If more ductility is required the copper is reduced to

about 5 per cent. but for some uses the copper is raised to 11 per cent. to produce sounder castings.

The most extensive investigation of the aluminum-copper alloys is that of Carpenter and Edwards and is reported in the Eighth Report of the Alloys Research Committee.¹ These investigators have covered the field very thoroughly including sand cast, chill cast and rolled material of various copper contents in their tests. For details the original report should be consulted but considerable of the data are given in the Bureau of Standards *Circular* referred to above.

Aluminum-Zinc.—The alloys of aluminum and zinc have been thoroughly investigated and reported upon by Rosenhain and



FIG. 32.—Microstructure of a fifteen per cent. aluminum-zinc alloy. (Archer.)

Archbutt in the Tenth Report to the Alloys Research Committee.² It was found that aluminum dissolves zinc in solid solution up to about 40 per cent. Consequently the aluminum-rich alloys used in engineering practice are simply solid solutions of zinc and aluminum, in which the zinc acts as a "stiffener" and increases the tensile strength and lowers the ductility. Reference to Fig. 29 shows that the effect of zinc, per cent. for per cent. up to 10 per cent. of the added element, is less than the effect of the other elements. This should have some commercial significance because it means that zinc will give less expensive alloys, but

¹ *Proc. Inst. Mech. Eng.*, 1907, p. 57.

² *Proc. Inst. Mech. Eng.*, 1912, p. 319.

the higher specific gravity and the greater difficulty in casting aluminum-zinc alloys offsets this to some extent. Another point in favor of the zinc alloys is that the elongation, for a given tensile strength, is greater than for the other alloys. The reason for this is to be found in the solubility of the zinc in the aluminum and the formation of characteristic solid solutions; other additions form brittle compounds which act more rapidly in lowering the elongation. The microstructure of the aluminum-zinc alloys is shown in Fig. 32.

The advantages of lower cost and higher tensile strength and elongation of the aluminum-zinc alloys, as compared to the aluminum-copper alloys, have appealed with greater force in England than in this country and we find the former more popular abroad and the reverse here. The alloy with two parts aluminum and one part zinc has a tensile strength of 35,000 pounds per square inch when sand cast and a specific gravity of about 3.3. The wrought alloy containing 26 per cent. zinc has a tensile strength of 62,000 pounds per square inch, a yield point of 56,000 pounds per square inch and an elongation of 16.5 per cent. on two inches. Alloys containing up to 15 per cent. zinc show satisfactory results when tested by the Izod single blow impact test and by Arnold's alternating stress test.

Aluminum-Magnesium.—Magnesium, like many other common metals, forms compounds with aluminum. The compounds with magnesium are said to be AlMg_2 and AlMg , melting at 455 and 462 degrees Cent. respectively.¹ These compounds are reported to form three eutectics as follows: magnesium- AlMg_2 , melting at 156 degrees Cent.; AlMg_2 - AlMg , melting at 445 degrees Cent.; and AlMg -aluminum, melting at 432 degrees Cent. Mercia states that magnesium is soluble at the eutectic temperature (450 degrees Cent.) up to about 13 per cent. The solubility decreases with the temperature to about 5 per cent. at 300 degrees Cent. and probably to still lower values at room temperature. Under normal conditions of cooling (sand casting) the eutectic enters at about 6 per cent. magnesium. The magnesium-rich phase is assumed by recent writers to be Mg_2Al_3 instead of MgAl .² It is now held that magnesium, at least when present in small amounts, unites with the silicon which

¹ GUILLET, *Alliages Metalliques*, p. 977.

² GRUBE gives Al_3Mg_4 , and the aluminum eutectic point at 35 per cent. Mg and 453 degrees Cent., *Zeit. anorg. Chem.*, 1905, Vol. 45, p. 225.

is present in the aluminum and forms the compound Mg_2Si .¹ This compound has a pronounced strengthening and embrittling effect, which is quite noticeable when even as small amounts as



× 250

FIG. 33.—Aluminum alloy with 1.7 per cent. Silicon and 4.5 per cent. Magnesium showing the $\text{Al-Mg}_2\text{Si}$ eutectic. (*Archer.*)



× 250

FIG. 34.—Aluminum alloy containing 3 per cent. Iron showing needles of FeAl_3 . (*Archer.*)

0.25 per cent. are present. The appearance of an alloy containing Mg_2Si is shown in Fig. 33.

¹ The compound Mg_2Si was identified by VOGEL; *Zeit. anorg. Chem.*, 1909, vol. 61, p. 46.

Aluminum-Iron.—Iron and aluminum form a compound FeAl_3 which occurs in the form of needle-like crystals or platelets as shown in Fig. 34. The solubility of iron in aluminum is very low. The presence of these hard crystals is not necessarily dangerous and iron, in small quantities in alloys of copper and aluminum, may improve the ductility. In casting practice a small amount of iron is an advantage as it decreases the shrinkage. The aluminum-iron system was reported upon by Gwyer.¹

Aluminum-Nickel.—Nickel and aluminum produce alloys with valuable properties but there seems to be no practical reason for using nickel in place of the less expensive copper. Consequently these alloys have gained no commercial importance. Suffice it here to refer to the extensive investigations by Read and Greaves of the light aluminum alloys containing nickel and nickel plus copper.² Hanson and Archbutt recommended etching with a 10 per cent. caustic soda which darkens the NiAl_3 ; CuAl_2 is not affected by this reagent. The hot 20 per cent. nitric acid is also useful in distinguishing between NiAl_3 and CuAl_2 as it gives the reverse action to that of the caustic soda. FeAl_3 and NiAl_3 are difficult to distinguish from each other.

Aluminum-Silicon.—Alloys of aluminum and silicon have no commercial importance. It has been shown that these two metals form a simple eutectiferous series with a eutectic at 10 per cent. silicon which melts at 578 degrees Cent.³ In other words, silicon is not present in aluminum as a compound of aluminum.

Aluminum-Manganese.—Manganese behaves similarly to iron in aluminum and forms the compound MnAl_3 which has the appearance of FeAl_3 under the microscope. This compound is practically insoluble in aluminum.⁴ Manganese is added at times to aluminum in amounts up to 2 per cent. for the purpose of increasing the strength, especially at high temperatures, and for non corrosive qualities. Hanson and Archbutt state that MnAl_3 occurs in some of the copper alloys in the form of well-defined cubes.

¹ GWYER, *Zeit. anorg. Chem.*, 1908, Vol. 57, p. 113.

² READ and GREAVES, *Journ. Inst. Met.*, 1915, No. 1, p. 100.

³ FRAENKEL, *Zeit. anorg. Chem.*, 1908, Vol. 58, p. 154; ROBERTS, *Trans. Chem. Soc.*, 1914, Vol. 105, p. 1383.

⁴ HINDRICH, *Zeit. anorg. Chem.*, 1909, Vol. 59, p. 414. This compound has been verified by ROSENHAIN and LANTSBERY by thermal and microscopical analysis. *Ninth Report*, p. 252.

Aluminum-Copper-Zinc.—In the Tenth Report to the Alloys Research Committee, Rosenhain and Archbutt describe the properties of an alloy containing 25 per cent. zinc and 3 per cent. copper, remainder aluminum, which was found to have exceptional properties. The tensile strength of this alloy is 41,000 pounds for sand castings and 45,000 pounds, per square inch, for chill castings, while the ductility is very low. In the hot rolled condition this alloy has the remarkable properties of 60,000 pounds for the yield point, 71,000 pounds per square inch for the tensile strength and 21 per cent. elongation on one inch. The material was tested in the form of a $\frac{1}{2}$ inch round bar. Cold drawing still further increases the tensile strength and gives a "specific tenacity" of 279, as compared with 231, the best value for the binary alloys of aluminum and copper. The alloy is structurally similar to the aluminum-zinc solid solutions. With the plant at their disposal the authors found some difficulty in rolling this alloy but they stated their conviction that, with suitable means, the alloys could be rolled commercially.

Alloys of aluminum, copper and zinc containing up to 23 per cent. zinc and up to 5 per cent. copper are used for automobile and aircraft castings, such as crank cases, and also for die castings.

Duralumin.—Duralumin is a quaternary alloy of aluminum and will be considered under forging alloys.

Casting Alloys.—The light alloys of aluminum which are used for casting purposes are the aluminum-zinc and the aluminum-copper alloys to which third or fourth metals may be added for certain improvements. The former are more generally used in this country principally because they give less trouble in casting. The zinc alloys give more shrinkage and are more tender while hot but their higher specific tenacity and greater ductility should give them an advantage for use in the higher grade castings.

Three of the common aluminum-copper compositions contain 5 per cent. copper, 8 per cent. copper (S.A.E. No. 30) and 12 per cent. copper (S.A.E. No. 32). The physical properties of these alloys are given in Fig. 29. The 5 per cent. alloy is used for automobile bodies which must have sufficient ductility to be bent cold into shape. The 8 per cent. alloy is the one which is so extensively used in this country for the automotive and allied industries, and for general industrial purposes, such as vacuum sweeper parts, etc. A modified composition contains 7.5 per cent.

copper, 1.5 per cent. zinc, and 1.2 per cent. iron. It has somewhat greater strength and ductility than the simple alloy, due largely to the FeAl_3 constituent. The 12 per cent. alloy when cast is quite dense and is particularly useful for engine cylinders and small parts which must be water tight.

The alloy which is used for pistons contains 10 per cent. copper, 1.25 per cent. iron and 0.25 per cent. magnesium. It is chill cast in permanent molds and gives good bearing surfaces. This alloy is also used for miscellaneous bearings against hard steel.

The alloy which is used in England for general casting purposes contains 13.5 per cent. zinc and 2.75 per cent. copper. As sand cast it has an average tensile strength of 25,000 pounds per square inch and an elongation of 1 per cent. or more. The specific gravity is about 3.0. As chill cast, the tensile strength is higher and the elongation is about 4 per cent. It is used for about the same purposes as our 8 per cent. copper alloy. Rosenhain and Archbutt state that the zinc alloys should be poured at a temperature about 50 to 60 degrees Centigrade above the melting point and that with reasonable care they may be easily cast. They give no information with which a comparison with the copper alloys can be made. As for strength *vs.* weight, they state that the zinc alloys have a maximum specific tenacity of 126 at 26 per cent. zinc as compared to 99, which is the maximum specific tenacity of the copper alloys.

A quaternary alloy of aluminum, zinc-copper and iron has been recently developed in America giving an average tensile strength of 27,500 pounds per square inch and an average elongation of 4.5 per cent. when cast in sand. It contains 7 per cent. zinc, 2.75 per cent. copper and 1.5 per cent. iron. It has an unusual combination of strength and ductility.

An alloy containing 5 per cent. magnesium and the remainder commercial aluminum, known as "magnalium," has been used somewhat where extreme lightness and ease of machining are the important considerations, for example for starting motor frames. Its specific gravity is 2.47, its tensile strength is 27,000 pounds per square inch and its elongation is about 3 per cent. It should be remarked, perhaps, that the use of alloys containing up to 30 per cent. magnesium has been noted. They are exceptionally light and strong and can be easily cast. Zimalium is a somewhat similar alloy containing zinc in amounts up to 20 per

cent. and magnesium in amounts up to 10 per cent. It is said to be easily worked and to be twice as strong as aluminum.¹

Manganese is added at times to pure aluminum or to a 2 per cent. copper alloy in amounts of 1 to 2 per cent. for light castings. The manganese gives the casting the necessary strength and does not detract materially from the resistance to corrosion possessed by pure aluminum. Small quantities of these alloys have been used for gun sights, optical instruments, parts of machinery used in the manufacture of chemicals, etc. The alloy with 2 per cent. copper and 1 per cent. manganese has a tensile strength of 18,000 pounds per square inch and an elongation of 8 per cent. but its proportional limit is only 2,000 pounds per square inch.

Table 12 is added as a summary of the properties of commercial castings, according to Rollason.

TABLE 12.—PROPERTIES OF COMMERCIAL CASTINGS. ROLLASON

	No. 12	S. A. E. 32	British L-5	Lynite 145
Tensile strength				
Pounds per sq. in.	20,000	20,500	25,000	27,500
Per cent. Elong.	1.5	0.5	1.5	4.5
Brinell hardness.	65	70	80	65
Scleroscope no.	14	16	18-20	14
Specific gravity	2.84	2.90	2.92	2.89
Copper, per cent.	8	12	2.5-3	3
Zinc, per cent.	12-14	7
Iron, per cent.	1
Magnesium, per cent.

High Temperature Alloy.—The general tendency of aluminum and its alloys is to become weaker and more ductile with rise of temperature, as is shown by the dotted line in Fig. 35. It has been found by adding 10 to 12 per cent. copper and 1 per cent. manganese to aluminum that an alloy is obtained whose properties scarcely change up to 250 degrees Cent. The solid lines in Fig. 35 represent the changes in strength and ductility of this alloy with increase in temperature up to 350 degrees Cent.

Effect of Thickness of Section.—Jeffries and Archer have shown that the tensile strength and elongation of aluminum castings decrease as the thickness of the section increases, and that the

¹ *Journ. Inst. Met.*, 1918, No. 2, p. 331. (Abstract.)

variation is practically linear.¹ For the 8 per cent. copper alloy the tensile strength and elongation drop from 25,000 pounds and 3 per cent. for $\frac{1}{4}$ inch test bars, to 14,000 pounds and under 1 per cent. for $1\frac{1}{2}$ inch test bars. Small test bars machined

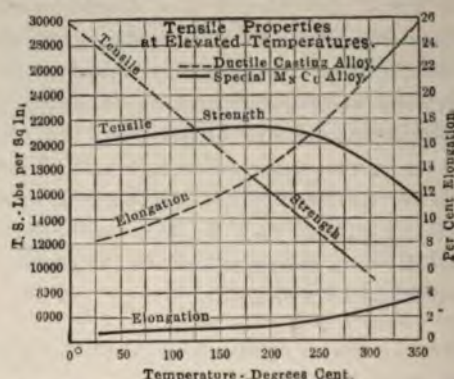
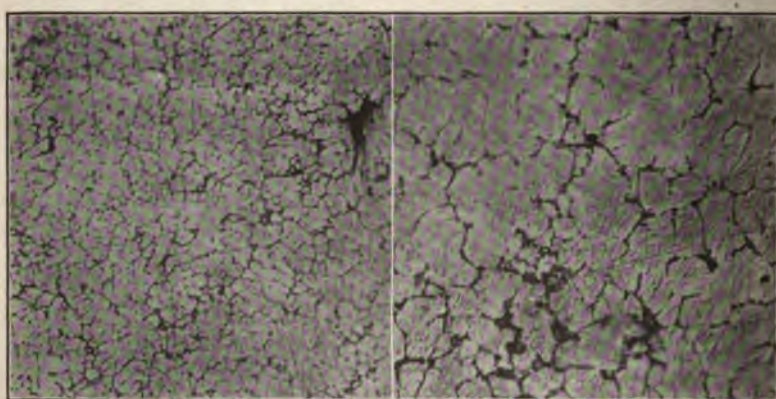


FIG. 35.—Physical properties of an alloy with 10 per cent. copper and 1 per cent. Manganese (solid lines). (Rollason.)

from the $1\frac{1}{2}$ inch bars averaged more than 19,000 pounds tensile strength and over 1 per cent. elongation. The tensile strength



Eight per cent. copper alloy cast as a $\frac{1}{4}$ inch bar. (Archer.) Eight per cent. copper alloy cast as a $1\frac{1}{2}$ inch bar. (Archer.)

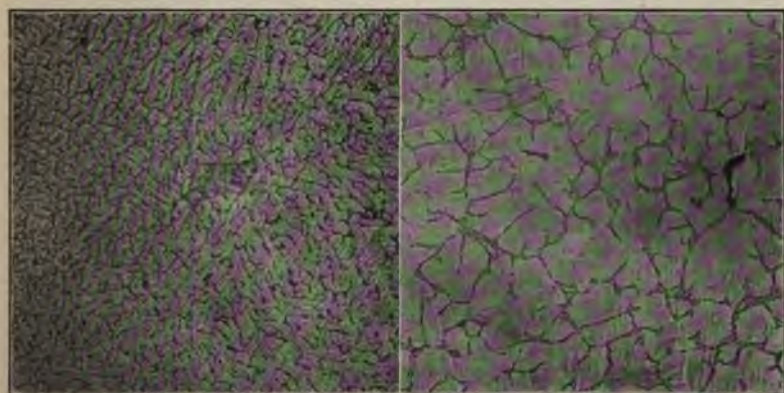
FIG. 36.

of the corresponding zinc alloy drops from 30,500 pounds for a $\frac{1}{4}$ inch test bar to 19,000 pounds for a $1\frac{1}{2}$ inch test bar. The

¹ Private communication.

elongation was also found to decrease as the diameter of the bar increased. In this case, however, small bars machined from the 1½ inch bar gave about the same results as the full sized bar. Jeffries and Archer remark, regarding the reason for this variation in properties, that the smaller bars are finer grained and of more favorable structure and that they are better fed during pouring than the larger bars. The effect of thickness of section on the structure is shown in Fig. 36.

Effect of Chill.—Jeffries and Archer have also shown that the effect of casting an aluminum alloy in a chill is to increase the tensile strength and elongation and to produce a much finer struc-



×50
Eight per cent. Copper alloy cast
in an iron mold—diameter $1\frac{1}{4}$ inch.
(Archer.)

× 50
Eight per cent. Copper alloy cast
in green sand—diameter $1\frac{1}{4}$ inch.
(Archer.)

FIG. 37.

ture. Thus the 8 per cent. copper alloy, when cast in a small section in a chill mold, may have a tensile strength of 31,000 pounds and an elongation of 6 per cent. Fig. 37 shows the difference in structure obtained by casting a cylinder $1\frac{1}{4}$ inches in diameter in an iron mold and in green sand. Chill casting practice is feasible, even highly desirable, when the solidification shrinkage is provided for and may be relied upon materially to improve the quality of the product.

Elastic Properties of Aluminum Alloys.—A typical stress-strain diagram of an alloy containing 8 per cent. copper is shown in Fig. 38. The proportional limit is seen to be quite low, about 5000 pounds per square inch, although the deformations are not

excessive above this load until the yield point at 11,000 pounds is reached. At the yield point selected the deformation is four times as rapid as at the proportional limit. The modulus of elasticity may be said to vary between 8,500,000 pounds and 11,000,000 pounds per square inch but it is generally about 10,000,000 pounds. Aluminum alloys are apparently better able to resist fatiguing strains at loads above their proportional limits than steel is, probably because they have no sudden yielding or break-

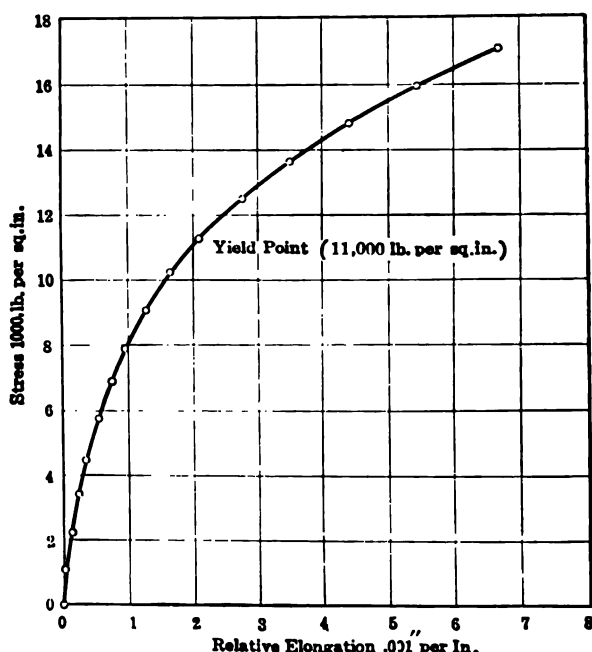


FIG. 38. Stress-strain diagram of aluminum alloy. Composition: 8 per cent. copper, rest aluminum. Properties: Y. P. 11,000 lbs. per sq. in., T. S. 22,800 lbs. per sq. in., Elong. 1 per cent. on two inches, R. A. 0.36 per cent.

ing down point. Jeffries reports 500,000 reversals at $\pm 14,000$ pounds per square inch and 16,000,000 reversals at $\pm 8,500$ pounds per square inch with a sand cast, 8 per cent. copper alloy. The proportional limit was about 5,000 pounds per square inch. The chill cast alloys are said to give even better results. Prof. Lea found that the 12 per cent. copper alloy withstood 12,000,000 reversals at $\pm 6,000$ pounds per square inch although the proportional limit was 5,000 pounds per square inch.¹

¹ Royal Automobile Society, 1919.

Forging Alloys.—The mechanical working of aluminum alloys, except for some small amount of bending for fabricating purposes, is largely limited to hot working. Some small amount of cold work occasionally may be done during the later stages. It is true that cold worked aluminum is used in light weight construction but the material used is mostly un-alloyed aluminum. Hot working aluminum alloys may be said to center about the alloy known as "duralumin," an alloy which is exceptional among the non-ferrous alloys in that its properties can be materially improved by heat treatment.

Duralumin contains about 3.5 to 5.5 per cent. copper, about 0.5 per cent. magnesium and at times small amounts of iron, manganese and even chromium and molybdenum.¹ This alloy can be hot worked by any of the standard methods and when so worked and allowed to cool normally to room temperature, its properties are not greatly different from those normal to the composition. If the alloy is reheated to 500 degrees Cent. and quenched in water, it commences at once to harden and after about four days its tensile strength has increased to 55,000 to 60,000 pounds per square inch and its elongation to 15 to 20 per cent. on two inches. At 100 degrees Cent. the hardening effect takes place more rapidly. This change in properties with time is generally referred to as "aging." The valuable properties which can be produced in duralumin by heat treatment has lead to its use as connecting rods in gasoline engines and in airplane construction.²

The explanation of the effect of quenching and subsequent aging of duralumin seems to be associated with the change in solubility of CuAl_2 from 500 degrees Cent. down to room temperature, see Fig. 30. If the alloy is quenched from 500 degrees or above, the segregation of CuAl_2 is inhibited, or at least temporarily suspended, while the gradual precipitation of the compound is responsible for the improvement in properties on aging. This is in brief the view advanced by Merica, Waltenberg and Scott³ who made the following observations concerning the

¹ These alloys were first investigated by Wilm in 1903 and described by him in 1911; see *Metallurgie*, Vol. 8, pp. 225 and 650. The microstructure and the structural relationships of the ternary alloys have been given by Vogel, *Zeit. anorg. Chem.*, 1919, Vol. 107, p. 265.

² ROLLASON. Alloyed Aluminum as an Engineering Material.

³ Bull. Amer. Inst. Min. Met. Eng., June, 1919. See also GRARD, *Compt. Rend.*, 1919, Vol. 169, p. 571.

phenomena in question.¹ Slow cooling to room temperature is not followed by the aging effect; while quenched alloys placed in liquid air likewise do not change with time. In one case there is no supersaturation while in the other, the temperature is too low to permit any change. Quenched alloys, if reheated immediately, show a heat effect at about 260 degrees Cent. Alloys after aging do not show this heat effect. This heat effect corresponds to the rapid precipitation of CuAl_2 . It was also concluded that a certain average size of particle of precipitated CuAl_2 produces the maximum hardness in duralumin. Thus aging at 200 degrees Cent. produces a greater hardness than aging at room temperature but after this maximum hardness (*i.e.* at 200 degrees Cent.) is produced, further duration of the time softens the alloy. This conclusion checks very well with the experimental data.² The addition of magnesium and other metals has the quantitative effect of improving the properties of heat treated duralumin but does not alter the mechanism of aging. There appears to be no advantage in substituting either nickel or manganese for the copper except that those alloys containing manganese have greater resistance to corrosion.³

The properties of commercial duralumin at different stages of manufacture can be summarized as follows, after Rollason.

TABLE 13.—PROPERTIES OF DURALUMIN. ROLLASON.

Condition	T. S.	Elong.	Remarks
Chill cast ingot.....	30,000	2	Low pouring temperature.
Forged; annealed.....	35,000	10-20	Varies with finishing temperature.
Quenched—500°C	55,000	20	After aging at room temperature.

T. S. in pounds per square inch.

Elongation in per cent. on two inches.

Duralumin is finding application in the manufacture of parts

¹ See also GUILLET, DURAND and GALIBOURG, *Compt. Rend.*, 1919, Vol. 169, p. 508.

² The micromechanism of aging of duralumin has been considered in some detail by JEFFRIES, *Journ. Inst. Met.*, 1919, No. 2, p. 329.

³ MÉRICA, WALTENBERG and FINN, *Bull. Amer. Inst. Min. Met. Eng.*, 1919, No. 151, p. 1051.

which can be rolled or forged and which should be light in weight. In the automotive industry this means connecting rods, rocker arms, etc. The fatigue resistance of duralumin makes it especially valuable for use in connecting rods. An interesting account of the use of duralumin in aircraft construction and a comparison with wood and steel is given in *Engineering*, beginning March 12, 1920, p. 357.

Heat Treatment of Aluminum Castings.—The success attending the heat treatment of forged duralumin has been so marked that work toward developing the heat treatment of aluminum alloy castings is encouraged. Work along this line has shown at least the necessity of heating and quenching so as to avoid oxidation of the inner surfaces of the pores which are invariably present in aluminum alloy castings. This has been accomplished by the Aluminum Manufactures Inc. by heating in fused nitre and quenching in oil. The work done so far has shown that the tensile strength can be increased by 0 to 40 per cent. and the elongation by 0 to 100 per cent. but it is of a preliminary nature and reference for details will be made to the work of Jeffries and Gibson.¹

The effect of temperature on heat treated duralumin is to lower the tensile strength and to increase the elongation, although the latter is not greatly affected up to 200 degrees Cent. Cohn found that the tensile strength drops from about 71,000 pounds to about 40,000 pounds at 200 degrees Cent. and to about 10,000 pounds at 300 degrees Cent.²

Summary.—We may say finally that the use of aluminum alloys depends upon the following factors. Foremost comes the low specific gravity of aluminum and its alloys, combined with which is a fairly high tensile strength. Parts made from aluminum and its alloys are both strong and light; also for a given rigidity aluminum will weigh less than any other metal used in engineering practice. The light weight of aluminum parts also means that the total weight of a structure can be reduced and that the unsprung weight and weight of the reciprocating parts can be made less than is customary. To secure these advantages it does not mean that the mechanical properties of the finished parts will be any less satisfactory than if made of heavier ma-

¹ JEFFRIES and GIBSON, *Bull. Amer. Inst. Min. Met. Eng.*, 1919, p. 2493.

² COHN, *Elektrotechnik u. Maschinenbau*, 1912, Vol. 30, pp. 809, 829; 1913, Vol. 31, p. 430. Ver. z. Foerd. d. Gewerbevereines, 1910, Vol. 89, p. 643.

terials. From the manufacturing point of view it is of interest to note that aluminum alloys can be machined about three times as rapidly as cast iron, which may be a vital consideration in lowering the manufacturing costs. Aluminum alloys can also be successfully used as bearings against hard metals. They are quite resistant to atmospheric corrosion and may be used as substitutes for brass and bronze; for equal volumes, aluminum is cheaper than either brass or bronze.

Ductility is a very important consideration here on account of the use of aluminum alloys in engineering structures. Whenever necessary, parts can be produced with sufficient ductility so that accidental overloading will be opposed by the deformation of the part. The assembling of aluminum castings is itself a procedure which may require considerable ductility.

CHAPTER IV

BRASSES AND BRONZES

THE BRASSES

Copper-Zinc Alloys.—The first general investigation of the brasses was that of Charpy in 1896,^{1, 2} who determined the microstructure and the mechanical properties of the copper-rich alloys containing up to about 50 per cent. zinc. Alloys containing up to about 35 per cent. zinc were found to consist of an agglomeration of polygonal crystallites each showing dendritic structure and varying in size with the rate of cooling. Alloys containing above 35 per cent. zinc were found to be composed of two different phases. The phase forming the ground mass was considered by Charpy to be amorphous. Alloys with 48 per cent. zinc were found to be coarsely crystalline and essentially different from alloys of the other two groups. The structures, as observed by Charpy, will be considered later. The alloy with 67 per cent. zinc was also found to be homogeneous and very brittle.

At this time Roberts-Austen determined the first complete freezing point curve of the copper-zinc alloys, as part of the work for the Fourth Report to the Alloys Research Committee.³ The liquidus and peritectic horizontals as determined by Roberts-Austen are essentially the same as now given in the constitution diagram and they will be considered later.

Of considerable interest is the line $e-e$ at 450°C. extending from about 25 per cent. zinc to 45 per cent. zinc and labelled "eutectic." This line was drawn on the basis of points observed on the cooling curves, which were made by the autographic recording device of Roberts-Austen, and were supposed to be due to the solidification of a eutectic, although no evidence was advanced, microscopical or other, with which to prove it.

¹ *Compt. Rend.*, 1896, Vol. 122, p. 670; also *Bulletin de Soc. d'Encouragement*, Vol. I, p. 180 (1896).

² Prior to this time copper and zinc had been found by WRIGHT in 1894 to be soluble in all proportions in the liquid state and the approximate location of the liquidus had been determined by GAUTIER in 1896.

³ *Trans. Inst. Mech. Engineers*, 1897, pts. 1-2, p. 31.

The presence of such a eutectic was immediately contested by Charpy who, in a second paper,¹ pointed out that the ground mass which would correspond to the eutectic, while undoubtedly fine-grained, still failed to exhibit the characteristic eutectic structure. The apparent discrepancy between thermal and microscopical evidence on this point has ever since been a subject of contention.

The first complete metallographical study of the copper zinc alloys was that of Shepherd in 1904.² His determination of the constitution diagram was based principally upon thermal

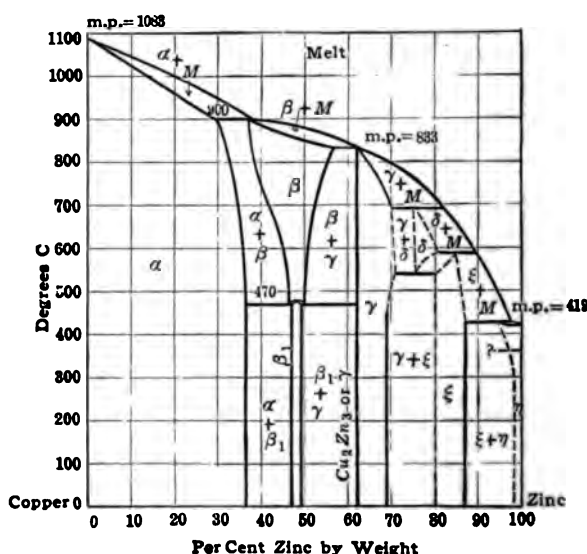


FIG. 39. —The copper-zinc constitution diagram.

and microscopical evidence. The liquidus and peritectic horizontals were determined from cooling curves and are as given in Fig. 39.³ It was not possible to determine the solidus with the same accuracy, on account of experimental difficulties, but it may be assumed that it is essentially as is given in the diagram.

¹ *Bulletin de la Soc. d'Encouragement* II, 1897, p. 414.

² *Journal Physical Chemistry*, 1904, Vol. 8, p. 421.

³ SHEPHERD's determination of the liquidus checks very well with other determinations of the liquidus, which were as follows: GAUTIER, 1896; CHARPY, 1896; ROBERTS-AUSTEN, 1897; SACKUR, 1905; TAFEL, 1908; and PARRAVANO, 1915.

It consists of six sloping branches, one for each of the solid phases which are in equilibrium with the melt.

The lines bounding the fields of the solid state were determined very accurately by annealing at various temperatures, to produce a stable structure, quenching to retain the structure, and microscopic examination to determine the constitution. Shepherd found from his annealing experiments that up to 37 per cent. zinc is held in solid solution in copper at room temperature but that the saturation concentration decreases with rise in temperature to approximately 30 per cent. at the peritectic temperature, 900°C. In the same way the lines bounding the β field were located.¹ The alloy with 60 atomic per cent. zinc, Cu_2Zn_3 , was found to be homogeneous and to have a constant melting point, similar to pure metals, at 833°C.² Shepherd failed to find the line $e-e$ of Roberts-Austen, either pyrometrically or micrographically, and he ascribed it to experimental error. On this account, the diagram was drawn with the β field extending down to room temperature, extending in width from 48 to 49.5 per cent. zinc. The alloys between Cu and Cu_2Zn_3 , being those of chief commercial importance, are the only ones which will be considered in detail.

The next work of importance on the constitution of the copper-zinc alloys was that of Guillet in 1906.³ Inasmuch as Guillet's work was largely a verification of that of Shepherd, it need not be considered here in detail. A further determination of the copper-zinc diagram was made by Tafel,⁴ but inasmuch as it too agrees with Shepherd's diagram, at least over the copper-rich range, it will not be considered in detail here. In particular, Tafel located the peritectic points by Tammann's method of thermal analysis and his determinations have been incorporated into the diagram of Fig. 39. Tafel likewise considered the line $e-e$ of Roberts-Austen and he, like Shepherd, decided that the heat effect must have been due to experimental error.

¹ The lines bounding the $\alpha + \beta$ field have also been accurately determined by MATHEWSON, *Jour. Amer. Inst. Met.*, 1918, Vol. 11, p. 12.

² SHEPHERD refused to regard the alloy Cu_2Zn_3 , or in fact any other alloy, as a compound but referred to them all as being solid solutions. This contention is not supported by other experimenters and it is now considered that Cu_2Zn_3 exists as an intermetallic compound.

³ *Rev. de Metallurgie*, 1906, Vol. 3, p. 243.

⁴ *Metallurgie*, 1908, Vol. 5, p. 342.

The Line e-e of Roberts-Austen.—The contraction of the β field with drop in temperature and the horizontal at 450°C . located by Roberts-Austen, led Guertler in his "Metallographie" to consider the possibility of a eutectoid, similar to that of the silver-cadmium system, although, from the microscopical study of these alloys, it seemed hardly possible to consider the constitution to be any other than that given by Shepherd in his diagram. This idea received independent support in 1911 when Carpenter and Edwards, for the first time since the work of Roberts-Austen in 1897, found heat effects in the copper-zinc alloys containing from 63 to 40 per cent. copper at about 470°C . by accurate pyrometrical work.¹ Their heating and cooling curves showed beyond reasonable doubt that there actually is a heat effect in these alloys in the solid state. To explain the presence of this heat effect, the suggestion was advanced that the β solid solution breaks down at 470°C . into an intimate mixture of α and γ , this mixture being ultra-microscopic so that the β constituent, while apparently homogeneous, is in reality heterogeneous. It was pointed out in the discussion that the explanation advanced by Carpenter and Edwards would find more ready acceptance if supported by microscopical evidence making it clear, even at low magnifications, that the "apparent β " constituent in reality consists of $\alpha + \gamma$.

To meet this criticism, Carpenter, in a second paper,² described annealing experiments designed to bring out the true duplex character of β . It was found that annealing an alloy lying well within the β field for six weeks just below the inversion temperature, or at 445°C . (boiling sulphur) caused no appreciable change in the microstructure which could be considered a coalescence of the particles of α and γ . Next, the same experiment was tried with two alloys, one containing a slight amount of excess α and the other a slight amount of excess γ , the small particles of the constituents in excess acting as nuclei to assist in the deposition or coalescence of α and γ , as the case may be. After several weeks annealing at 445°C ., two new constituents were found to form resembling α and γ in appearance and of such size as to be readily visible under low magnification. This experiment seemed to make it perfectly evident that the β constituent was composed of submicroscopic particles

¹ *Journ. Inst. Metals*, 1911, No. 1, p. 127.

² *Ibid.*, 1912, Vol. 7, p. 70.

of α and γ and that it was only apparently homogeneous. To make the demonstration even more conclusive, the samples were finally annealed for twenty-four hours at temperatures above 470°C. and slowly cooled. After this treatment the micro-sections exhibited their original appearance, that of so-called "apparent β ."

Carpenter later described further experiments on the structural resolution of the β constituent, dealing principally with the effect of third metals.¹ The critical point at 460°C. was again considered by Hudson² who contended that the heat effect must be due to a polymorphic transformation of the β constituent from β to β_1 and advanced evidence to support his contention. The diagram offered to explain this transformation as given by Hudson is reproduced in Fig. 39. The principal evidence advanced by Hudson was the formation of a constituent by annealing $\alpha + \gamma$ at temperatures below the critical point which was neither α nor γ and called β_1 . No positive evidence was advanced to show the polymorphic transformation in β , although, as the author points out, all the phenomena which he has observed can be explained on such a basis. Furthermore, this does not necessitate the assumptions regarding the tardy coalescence of two separate parts of β which were made necessary by Carpenter's work. With the exception of this point, the main features of the copper-zinc constitution diagram may be said to be well known.

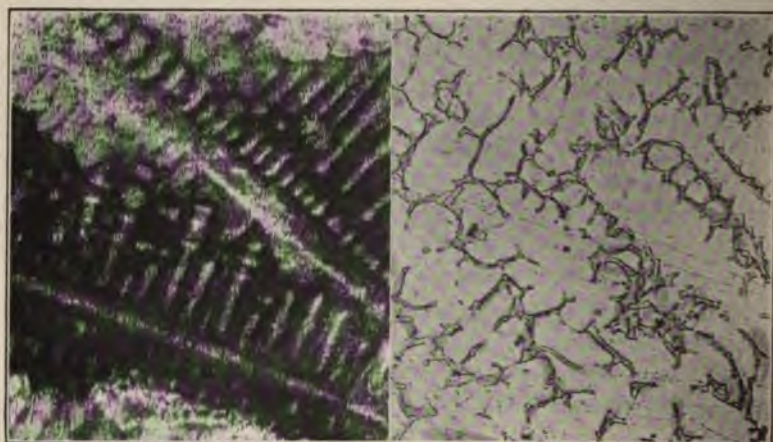
The difficulty of producing equilibrium in the copper-zinc alloys without volatilizing part of the zinc, has frequently been noted, and Tafel found that the alloys toward the middle of the series liquate considerably, so much so that chemical analysis is less accurate for determining the composition than the method of weighing before and after melting.

Microstructure.—The α solid solutions have structures characteristic of metallic solid solutions. In the cast state they show the customary dendritic structure. Annealing at temperatures above 700°C. produces uniform polygonal crystallites which show profuse twinning. Mechanical work elongates the grains, which may then be restored to their original polygonal condition by annealing, this time at temperatures considerably lower than 700°C.

¹ *Journ. Inst. Metals*, 1912, No. 2, pp. 51 and 59.

² *Ibid.*, 1914, No. 2, p. 89.

Alloys containing more than 35 to 37 per cent. zinc show two phases— α and β or, as Hudson states, β_1 , the amounts of which vary with the zinc content. The surface patterns exhibited by these alloys are of two different types, depending upon the genesis of the constituents. In the alloys containing just above the saturation concentration of zinc, the α phase is the first to form from the melt, while the β phase forms afterwards and must form interstitial filling matter for the α dendrites. As soon as more zinc is added the order of formation is reversed—the β forms directly from the melt and, with fall in temperature, the



×100

FIG. 40.

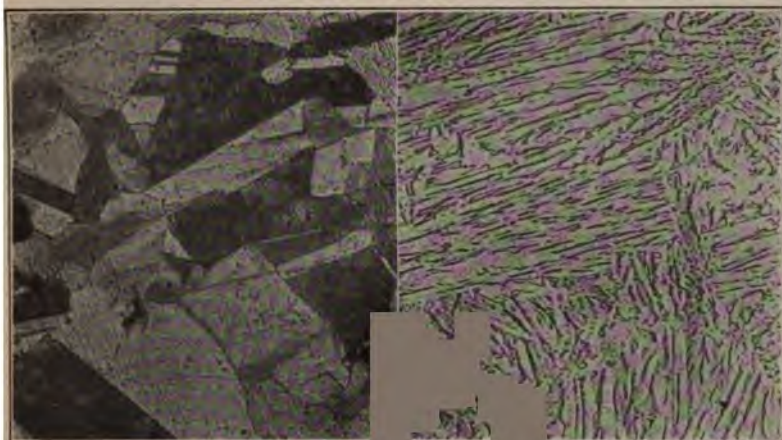
×100

FIG. 41.

FIG. 40.—Seventy per cent. copper, 30 per cent. zinc, cast in a warm mold. Etched with NH_4OH and H_2O_2 to show dendritic structure.

FIG. 41.—Sixty-three per cent. copper, 37 per cent. zinc, as cast. α dendrites and β_1 . Etched with Miller's reagent.

α phase separates as a segregate out of the β phase. This produces the Widmanstätten or segregate structure which is one of the commonest structures of commercial brass. At about 47 per cent. to 49 per cent. zinc, the alloys are homogeneous with a structure resembling that of homogeneous α ; but two of the commonest characteristics of α , the dendritic structure and twinning, have never been noticed. As soon as 50 per cent. zinc is reached, γ or Cu_2Zn_3 separates out with characteristic segregate structure. These structures are shown in Figs. 40 to 45.



×100
FIG. 42.

×100
FIG. 43.

FIG. 42.—Sixty-five per cent. copper, 35 per cent. zinc, annealed. Homogeneous α . Etched with ammonium chloride.

FIG. 43.—Sixty per cent. copper, 40 per cent. zinc, as cast. α segregate in β_1 . Etched with Miller's reagent.



×100
FIG. 44.

×100
FIG. 45.

FIG. 44.—Fifty-two per cent. copper, 48 per cent. zinc. β_1 . Etched with Miller's reagent.

FIG. 45.—Forty-eight per cent. copper, 52 per cent. zinc; etched with basic copper-ammonium chloride to show τ segregate in β_1 .

Physical Properties of Brass.—Electrical Conductivity: The addition of zinc lowers the conductivity of copper very rapidly so that the curve drops with the characteristic U-shape.¹ The α field, as determined in this manner, corresponds closely to that given in the constitution diagram.² Over the $\alpha + \beta$ portion of the diagram from 37 per cent. zinc up, the curve runs as a straight line to a maximum at about 47 per cent. zinc. From this maximum the curve again runs linear to about 57 per cent. zinc. The shape of the curve indicates the presence of a compound CuZn , or at least of a solid solution corresponding to β or β_1 , so that this curve offers strong evidence against the assumption of heterogeneous mixtures of α and γ phases over this range of composition.

Confirming these points, we have determinations of the specific conductivities and temperature coefficients. The temperature coefficient curve, in particular, passes through a sharp maximum at about 50 atomic per cent. zinc, while two other compounds, CuZn_2 and CuZn_6 , are indicated on the curve.³ Cu_2Zn_3 is brought out by a maximum on the resistance-concentration curve. β or β_1 has been regarded as a compound CuZn which is slightly dissociated at room temperature.⁴

¹ GUERTLER, *Zeit. anorg. Chem.*, 1906-07, Vol. 51 and Vol. 52, p. 397.

² Electrical conductivity-temperature curves for the Cu-Zn alloys have not been used for the investigation of the constitution, but it is interesting to note that LeCHATELIER (Contrib. a l'Etude des Alliages) published a curve of an alloy with 37 per cent. Zn which showed a transition point at 725°. This point corresponds fairly well with the temperature at which α just passes into solution in β on heating.

³ NORSA, *Compt. Rend.*, 1912, Vol. 155, p. 348. PUSCHIN and RJASCHSKY, *Journ. Russ. Phys.-Chem. Soc.*, 1905, Vol. 44; *Zeit. anorg. Chem.*, 1913, Vol. 82, p. 50.

⁴ For the chemical behavior of the copper-zinc alloys, see SACKUR, *Arch. k. Gesundheitsamt*, 1904, Vol. 20, p. 512 and Vol. 22, p. 127. SACKUR, MAUZ, and SIEMENS, *Ber. deut. Chem. Gesellschaft*, 1905, Vol. 38, p. 2186. LINCOLN, KLEIN and HOWE, *Journ. Phys. Chem.*, 1907, Vol. 11, p. 501. For electrolytic potential measurements, see LAURIE, *Journ. Chem. Soc.*, 1888, Vol. 53, p. 104. HERSCHKOWITCH, *Zeit. Phys. Chem.*, 1898, Vol. 27, p. 123. PUSCHIN, *Zeit. anorg. Chem.*, 1907, Vol. 56, p. 1. CAMBI, *Rend. r. Inst. Lombardo* (1915-2) Vol. 48, p. 826. For the electrolytic deposition of copper-zinc alloys, see FIELD, *Electrician*, 1909, Vol. 63, p. 632. BENNET and DAVISON, *Trans. Amer. Electrochemical Soc.*, 1914, Vol. 25, p. 347. For the heat of formation, see BAKER, *Phil. Trans. Royal Soc.*, 1901, Vol. 196, p. 529. According to the work of BAKER, the heat of formation of the Cu-Zn alloys is at a maximum at CuZn and CuZn_2 . For specific volume, see MAEY, *Zeit. Phys. Chemie*, 1901, Vol. 38, p. 204.

Mechanical Properties.—Mechanical properties of the copper-zinc alloys, as obtained by the United States Board and other experimenters, have been reported upon very thoroughly by Thurston.¹ Charpy has also given the tensile strengths and elongations of mechanically worked and “completely annealed” brasses containing up to 50 per cent. zinc. His results are reproduced in the form of curves in Fig. 46.² These curves show the improvement in properties obtained by adding zinc to copper, inasmuch as both the tensile strength and elongation are increased. Summarizing his work, Charpy stated that the elastic limit, resistance to penetration, and the stiffness, increase continuously with the zinc content, with the most rapid variation between 35 and 40 per cent. The compressive strength and the reduction of area decrease up to about 30 per cent. zinc and then increase up to 45 per cent. zinc. Fragility is negligible until the zinc amounts to 45 per cent. while the 50 per cent. alloy is so brittle that it is worthless for mechanical purposes. For commercial uses he recommends using less than 43 per cent. zinc but not more than 70 per cent. copper. In this range, considering completely annealed bars, one can secure brasses with properties varying from 60 per cent. elongation and 40,000 lbs. tensile strength to 54,000 lbs. tensile strength and 40 per cent. elonga-

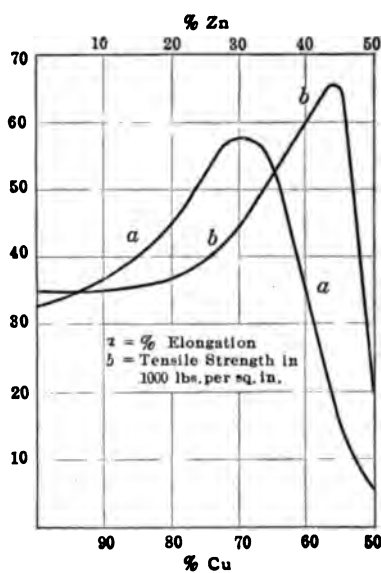


FIG. 46.—Tensile properties of annealed brass. (Charpy).

For the vapor pressure of zinc in brass, see JOHNSTON, *Journ. Amer. Inst. Met.*, 1917-18, Vol. 12, p. 15. For the thermal expansion of α and β brass, see MERICA and SCHAD, *Trans. Amer. Inst. Met.*, 1917-18, Vol. 11, p. 396. The linear coefficient of expansion may be taken as 0.18×10^{-4} for the lower temperatures.

¹ *Materials of Engineering*, Vol. 3 (1893).

² These results were confirmed by ROBERTS-AUSTEN in his report on the Cu-Zn alloys.

tion. By judicious working, the tensile strength can be increased to 85,000 lbs.

The tensile strengths and ductilities of chilled cast brass varying in composition from 47.5 to 100 per cent. copper have been studied by Lohr.¹ The tensile strength of the α brasses was found to be nearly constant. As soon as β enters, the tensile strength increases until the maximum of 71,000 lbs. per sq. in. is reached at approximately 55 per cent. copper. The maximum ductility obtained was 36 per cent. at 65 per cent. copper. By casting the metal within the range from 100 to 200°C. above the liquidus, castings could be obtained with properties varying between 71,000 lbs. tensile strength and 14.8 per cent. elongation and 36,000 lbs. tensile strength and 35.6 per cent. elongation. The alloys consisting entirely of β or of $\beta + \gamma$ have very low strength and no ductility. The tensile strength, hardness, and resistance to shock of a series of pure copper-zinc alloys have been determined by Guillet.² Guillet found for the annealed alloys that the hardness bears a direct relation to the tensile strength. The resistance to shock was found to be very high. The effect of cold working varies inversely with the elastic limit, the alloy with the lowest elastic limit undergoing the greatest change in properties. The hardness was increased by quenching, presumably by the formation and retention of β .

Brass rods, up to 2.5 inches diameter, are regularly produced in commercial practice having a yield point of 50 to 55,000 lbs. per sq. in., a tensile strength of 65 to 70,000 lbs. per sq. in., and an elongation on two inches of 25 per cent. The composition is approximately 60 per cent. copper, 40 per cent. zinc, with less than 1 per cent. lead. Brass cartridge metal with approximately 70 per cent. copper (± 1 per cent.), 30 per cent. zinc (± 1 per cent.), 0.75 per cent. lead and 0.25 per cent. iron, given a "light anneal" (about one hour at 500°C.) is produced with 55,000 lbs. per sq. in. tensile strength and an elongation on two inches of 45 per cent. These results are average results of a large number of tests.

The hardness of copper-zinc alloys has been given by Turner and Murray³ as determined by both scleroscope and Brinell

¹ *Journ. Phys. Chem.*, 1913, Vol. 17, p. 1. BANCROFT and LOHR; *Orig. Com. 8th Intern. Congr. Applied Chem.*, Washington, 1912; Division II, p. 9. An ingenious method of casting these alloys in a graphite mold is described.

² *Bulletin Soc. d'Encouragement*, 1914, Tol. 121, p. 14.

³ *Journ. Inst. Metals*, 1909, No. 2, p. 98.

methods. The hardness *vs.* composition curve showed a number of maxima and minima. In particular it was noted that the alloy with 40 per cent. copper is evidently a chemical compound.

The hardness of the copper-zinc alloys has also been given by Meneghini¹ using a modified Brinell testing machine similar to that described by Le Gris.² The results were obtained with

TABLE 14.—HARDNESS OF THE COPPER-ZINC ALLOYS

No.	Copper, per cent.	Zinc, per cent.	Diameter of impression, millimeters	Hardness, $\delta = \frac{P}{d}$
1	100.00	0.560	19.4
2	94.15	5.85	0.522	21.8
3	87.17	12.83	0.495	22.0
4	79.81	20.19	0.492	22.1
5	77.80	22.20	0.462	23.5
6	75.20	24.80	0.482	22.5
7	70.05	29.95	0.511	21.3
8	67.31	32.69	0.513	21.2
9	64.50	35.50	0.516	21.0
10	63.82	36.18	0.533	20.4
11	60.48	39.52	0.492	22.1
12	59.23	40.77	0.456	23.8
13	54.45	45.55	0.389	27.9
14	51.89	48.11	0.380	28.6
15	49.54	50.46	0.361	30.1
*16	45.20	54.80	0.247	44.0
*17	42.51	57.49	0.162	67.0
*18	33.65	66.35	0.150	72.5
*19	29.19	70.61	0.250	42.0
20	27.54	72.46	0.290	38.0
21	25.84	74.16	0.296	36.8
22	22.85	77.15	0.365	29.7
23	22.05	77.95	0.386	28.2
**24	15.13	84.87	0.454	24.0
25	9.63	90.37	0.437	24.9
26	8.33	91.67	0.447	24.3
27	4.25	95.75	0.456	23.8
28	3.60	96.40	0.465	23.4
29	100.00	0.685	15.9

$P = 10.870$ kilogrammes.

*For these specimens the determination was made with a stronger pressure.

**For a single impression.

¹ *Ibid.*, 1915, No. 2, p. 160.

² *Rev. de Met.*, 1913, Vol. 10, p. 1058.

13230A

a small ball (diameter = 2.9 mm.). The hardness number was taken as $\delta = \frac{P}{d}$ where P = the pressure in kgs. and d is the surface of the impression. Values for δ are given in Table 14.

Heat Treatment of Brass.—The heat treatment of brass, principally annealing after working, is an operation which has been, and still is in certain quarters, conducted with little attempt at scientific metallographic control. It is, of course, well known that brass must be annealed during the processes of cold rolling, or otherwise shaping, to relieve internal strains and to put the material in condition for further working or to make it fit for service. In Charpy's early work on brass, already cited, it was demonstrated that cold worked brass (which was consequently abnormally strong and brittle) when reheated to gradually increasing temperatures, became softer and more ductile. Charpy noted that the reheating must be carried up to a certain minimum temperature in order to produce any appreciable change in the properties. This minimum temperature, he said, depended

TABLE 15. —EFFECT OF ANNEALING COLD-WORKED BRASS

Annealing temperature, °C.	Pure copper		18.4 per cent. Zn		30.2 per cent. Zn		40.4 per cent. Zn	
	Tensile strength	Elongation	Tensile strength	Elongation	Tensile strength	Elongation	Tensile strength	Elongation
	No. 1		No. 6		No. 7		No. 8	
0	42,670	1.66	59,400	2.2	70,400	1.1	77,000	3.5
150	59,870	3.0	71,116	1.4	78,300	9.1
200	43,800	1.4	59,400	0.8	72,600	1.1	73,650	6.0
280	43,380	1.1	57,000	1.2	66,100	3.1	74,680	13.9
420	32,000	32.0	28,800	78.1	48,350	26.0	59,280	27.6
500	31,500	33.3	40,800	35.3	48,350	31.6	55,470	33.3
560	32,300	32.5	39,100	43.5	42,670	35.3	54,900	38.6
600	31,500	33.0	40,700	42.7	39,100	29.4	55,470	33.0
650	31,500	29.7	54,049	34.9
730	31,500	27.2	30,500 +	16.5 +	41,600	51.3	58,315	30.6
780	31,291	32.5	40,700	52.2	53,300	37.6
800	29,200	27.8	28,000 +	17.4 +	40,700	65.3	49,000	34.7
830	31,291	33.5	37,100	42.2	39,100	47.8
900	29,500	33.3	31,300	44.4
940	30,200	34.1	35,300	40.3
1000	27,300	30.0

NOTE.—The impurities were Sn, Pb and Fe, amounting to 0.3 to 0.4 per cent. The test specimen was 55 mm. in diameter and 90 mm. long (parallel section). Temperatures were measured with a Le Chatelier thermocouple, calibrated by the fixed points—m.p. of gold = 1045°C. and b.p. of sulphur = 448°C.—temperatures assumed to be proportional to galvanometer deflection.

Contribution à l'Etude des Alliages, p. 47.

On the extent of the "work" and was higher for materials which has smaller amounts of work done on them. He noted that this temperature was lower for the brasses with high zinc but considered this was because the same treatment resulted in a greater amount of "work." His results for several alloys are given in Table 15.

The Heat Treatment of Muntz Metal.—The heat treatment of Muntz Metal (60 per cent. copper, 40 per cent. zinc) has been reported upon in considerable detail by Bengough and Hudson.¹ This alloy consists of α and β so that it is possible, by heat treatment, to vary their relative amounts and distribution and, therefore, the mechanical properties of the alloy. In their work, the effect of time as a factor influencing the microstructure and the properties was taken into consideration. It was suggested that heating to too high temperatures followed by too rapid cooling might, by the retention of β , be one of the causes of "burning" Muntz metal.

Summing up their work on impact tests with the Izod machine, Bengough and Hudson were of the opinion that the results were not sufficiently discriminating to be of great importance. Four different types of microstructure were reported, depending principally upon the annealing temperature. The rolled bar showed the typical elongated structure in the longitudinal section and was fine grained. This structure was not changed by annealing below 500°C. At this temperature the annealing commenced to alter the structure by increasing the grain size and by effacing

TABLE 16.—EFFECT OF ANNEALING COLD-WORKED MUNTZ METAL

Type of structure	Approximate temperature limits of annealing alloy, °C.	Maximum stress, lbs. per sq. in.	Elongation, per cent. on 2 in.
Rolled.....	0-500	69,440-61,500	Hard rolled 37-50 Soft rolled 47-65
Island.....	500-575	Hard rolled 58,240-53,760 Soft rolled 58,240-47,040	Hard rolled 52-60 Soft rolled 55-65
Network.....	575-790	Hard rolled 52,600-50,400 Soft rolled ?	Hard rolled 50-57 Soft rolled 65-72
Cast.....	790-895	Hard rolled 52,600-50,400 Soft rolled 47,040-44,800	Hard rolled 17-44 Soft rolled ?-72

¹ *Journ. Soc. Chem. Ind.*, 1908, Vol. 27, pp. 43 and 654.

the rolled structure of the longitudinal section. Heating to higher temperatures produced the typical cast or Widmanstätten structure which is caused by the separation of α from β . They give as a summary of their results, a table reproduced in Table 16 from which may be obtained the effect of annealing temperature on the microstructure and static properties of rolled Muntz metal.

Grard conducted a systematic investigation of the effect of mechanical working and annealing on the properties and microstructure of brass, such as is used for cartridge cases, with 67

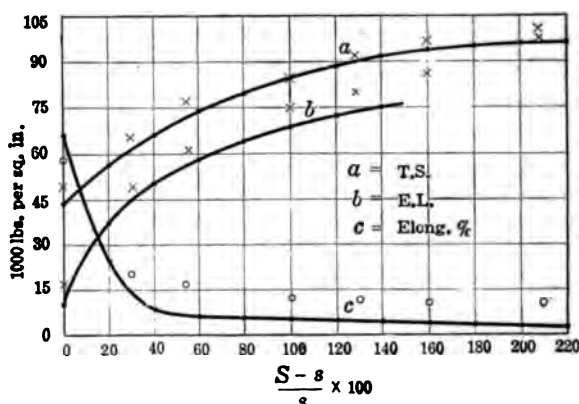


FIG. 47.—Effect of cold work on the tensile properties of cartridge brass, containing 67 per cent. copper and 33 per cent. zinc. S = original cross section and s = final cross section. (Grard.)

The results of Ellis for a pure grade of 61:39 brass are also plotted: X = T. S. and Y , P , and O = elongations for a gage length = $4\sqrt{\text{area of specimen}}$. See *Journ. Inst. Met.*, 1919, No. 1, p. 323.

per cent. copper and 33 per cent. zinc.¹ The variations of the tensile strength, and elastic limit as determined by extensometric measurements, and elongations of the 67/33 brass, produced by varying degrees of cold work, are given in Fig. 47. The abscissæ represent the amount of work done as determined by the reduction of the cross sectional area = $\frac{S-s}{s} \times 100$, where S = the original cross section and s = the final cross section. The test bars were either 6×10 mm. or 0.3×14 mm. with a gage length of 100 mm. The bars before rolling were “annealed” and of such dimensions that by reducing the thickness to either

¹ *Rev. de Metallurgie*, 1909, Vol. 6, p. 1069.

6 mm. or 0.3 mm. the desired degree of cold work would be accomplished. The elastic limit was determined by noting the first load which would produce permanent set in the material. The method used permitted measurements of the gage length (100 mm.) to 0.001 mm.

The effect of annealing for thirty minutes at successively increasing temperatures, on the mechanical properties is given in Fig. 48. This figure shows the sudden change from the cold worked state to the partially annealed state in the temperature interval from 250° to 350°C. and the more gradual change as the annealing temperature is carried on up to 800°C. which is the temperature of complete annealing. Higher annealing temperatures produce the deterioration which has been called "burning."

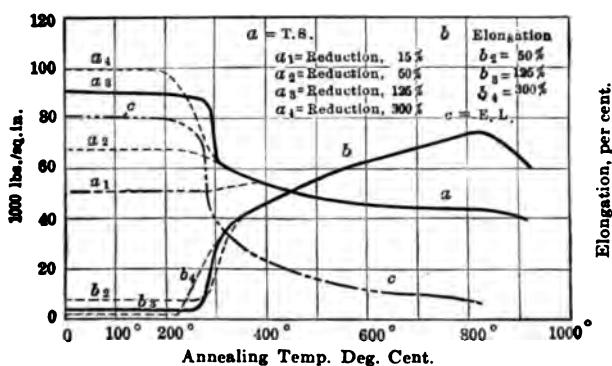


FIG. 48.—Effect of annealing cartridge brass which has been cold worked by various amounts. The time of annealing was 50 minutes. (Grard.)

The microstructure was closely followed and was found to furnish a reliable index to the physical condition of the material. The over-annealed brass was found to contain blowholes and to have a structure similar to that of cast brass. The great importance of the use of the microscope in connection with the rolling and annealing of brass for the purpose of determining its condition is pointed out. This point has been given considerable attention in recent years and will be more fully discussed in Part III, along with the use of the Brinell test as a means of following the annealing process. There is some doubt as to the value of the Brinell test as a means of following the cold working of brass as Portevin, confirming Grard and Guillet, found that the Brinell number increased rapidly with the first reductions (10

to 20 per cent.), after which the change was very much less.¹ Ellis, on the other hand, found a fairly regular increase in Brinell hardness of 61:39 brass from 77 up to 194 at 75 per cent. reduction by cold rolling. The anomaly noted by Alkins for copper, was found to occur at 56 to 62 per cent. reduction over which range the Brinell hardness number was 181.²

Bengough and Hudson continued their investigations on the heat treatment of brass on a 70/30 mixture containing very small amounts of impurities.³ Their work largely confirmed that of other experimenters on this alloy. They showed, in particular, the relatively greater effect of annealing on the yield point as compared to the tensile strength. It was found that the time of annealing becomes relatively important as the temperature is increased, although annealing twenty-four hours at 810°C., while it produced a further lowering of the tensile strength as compared to 30 min. did not cause "burning."

Tests at temperatures up to 600°C. were carried out to compare the results with those obtained on annealed bars. There was found to be a gradual falling off in the tensile strength from 58,240 lbs. at room temperature to below 4,480 lbs. at 600°C.; the elongation dropped at the same time from about 16 per cent. to below 2 per cent. at 415°C. but it was found to increase to 15 per cent. and above at higher temperatures from 450° to 600°.

The recrystallization and coalescence of the grains was closely followed under the microscope. Annealing a half hour at 500°C. produced a finer grained material than the original, suggesting that crystallization sets in from numerous new crystal nuclei. Over-annealed brass was found to be very coarsely crystalline, while essentially the same was true for burnt brass. It was also found that, in burnt brass, the lead segregates to the crystal boundaries and is indicated by more or less rounded particles distributed throughout the bar.

The authors point out that the best combination of strength and ductility appears to be obtained by annealing between 600° and 700°C. Small quantities of impurities, usually introduced with the zinc, have an important technical effect by increasing the tendency to burn. This is in accordance with the work of Charpy. The loss of zinc by volatilization during the annealing

¹ PORTEVIN, *Rev. de Met.*, 1919, Vol. 16, p. 235.

² ELLIS, *Journ. Inst. Met.*, 1919, No. 1, p. 319.

³ *Journ. Inst. Metals*, 1910, No. 2, p. 92.

process, while appreciable, is mainly a surface effect and is not considered to be the cause of burning.¹

In an elaborate series of tests on brasses of the α type it has been shown that heating to temperatures within the $\alpha + \beta$ field, followed by quenching to preserve the β net work, results in a material strengthening of the alloy. For the 65:35 brass, this treatment increased the tensile strength by 10,000 pounds per square inch, and lowered the elongation by 15 units. This treatment may be followed by a second and lower heating to produce a partial absorption of β which increases the elongation but does not materially affect the strength, or a small amount of work may be used to raise the strength. In this way the quenched alloy can be made considerably stronger and only slightly less ductile than the plain α alloy. Homogeneous α can be reproduced by heating for a half hour at a low red, or by heating to a higher temperature and cooling, the 70:30 brass in air, the 67:33 brass at 50°C. per minute, and the 65:35 brass at 10°C. per minute.²

The heat treatment of Muntz metal in cold drawn one-half inch round bars was again reported upon by Stead and Stedman.³ The bars were heated for forty-eight hours at temperatures between 470° and 860°C., one set being quenched and the other set slowly cooled from the annealing temperature. The time of annealing, forty-eight hours, is so long that the results are not directly applicable to technical practice, but for this length of time it was found dangerous to anneal between 750°C. and 800°C. because the β crystals become enveloped by the α phase, which is said to be conducive to weakness in both the quenched and air cooled brasses. The β constituent, when retained by quenching from within the β field, has a tenacity of about 64,960 lbs. per sq. in. as compared with 58,240 lbs. per sq. in. when annealed at 500°C. An interesting case of reabsorption was brought out by the microscopical examination, and its effect on the mechanical properties was shown to be quite pronounced. Up to about 600°C. the only effect of annealing was to increase the size of the α and β particles; above this temperature a cer-

¹ The distillation of zinc from copper-zinc alloys when heated in a vacuum has been investigated by THORNEYCROFT and TURNER, *Journ. Inst. Metals*, 1914, No. 2, p. 214.

² MATHEWSON and DAVIDSON, *Trans. Amer. Inst. Met.*, 1917, Vol. 11, p. 12.

³ *Journ. Inst. Metals*, 1914, No. 1, p. 119.

tain amount of α is reabsorbed by the β , in accordance with Shepherd's constitution diagram, which, on quenching, is retained in super-saturated β . On slow cooling the reabsorbed α again separates out as a segregate giving what appears to be two generations to the α (1) large unabsorbed α crystals and (2) small segregate α crystals. This effect was noticed up to 773°C. The quenched alloy shows β crystals surrounded by envelopes of unabsorbed α . The slowly cooled alloy shows the same α envelopes in a matrix of α segregate and β . This is the structure which exhibited the low elongation, 38 per cent., and reduction of area, 44 per cent. Heating to 812°C. caused a complete reabsorption of α so that, on cooling, only the α segregate and β were present, as a mixture, which was finer grained than the material heated to 500° to 600°C. This recrystallization resulted in an improvement in the properties. The mechanical properties obtained are given in Table 17.

TABLE 17.—EFFECT OF ANNEALING COLD-DRAWN MUNTZ METAL

Mark	Heat treatment		Quenched in water				Cooled in air			
	Temp. Deg. C.	Duration	Y. P.	T. S.	Elong. per cent., 1 in.	R. A., per cent.	Y. P.	T. S.	Elong., per cent., 1 in.	R. A. per cent.
Normal bar of										
A & B							34	58	44	54
A	270	984 hrs.	30	57	54	63
B	430	3 mos.	25	51	56	63.4
Hard drawn							82	87	19	54
1	475	48 hrs.	35	58	45	66.2	33	56	50	65.6
2	565	48 hrs.	33	57	41	58.8	30	56	51	63.1
3	675	48 hrs.	32	64	38	43.8	30	59	47	58.8
4	720	48 hrs.	35	61	26	37.8	27	54	40	48.6
5	749	48 hrs.	43	64	20	32.6	32	58	42	43.8
6	773	48 hrs.	45	51	10	26.6	30	56	38	43.8
7	812	48 hrs.	43	65	25	26.0	29	57	48	53.9
8	833	48 hrs.	43	65	26	37.8	28	56	45	48.6
9	860	48 hrs.	41	60	30	32.1	33	54	48	58.2

Y. P. and T. S. in 1,000 pounds per square inch.

Guillet conducted a systematic investigation of the properties of brass containing from 56 to 100 per cent. copper, and the effects of rolling, drawing, and heat treatment.¹ The copper

¹ *Rev. de Metallurgie*, 1914, Vol. 11, p. 1094.

and zinc used were exceptionally pure. The alloys were very carefully made and rolled either hot or cold, depending upon the composition. Guillet stated that the alloys for hot working contained between 90 and 100 per cent. copper and between 56 and 63 per cent. copper, while those for cold working contained more than 60 per cent. copper. With between 60 and 62 per cent. copper the brasses could be cold worked providing the reductions were correctly chosen. The alloys for hot working were cast in 30 kg. ingots 90 mm. in diameter, rolled in one train and six passes to 40 mm. and in the finishing train to 22 mm. in six passes. Certain of the bars were drawn to 20 mm. The alloys for cold working were cast in 10 kg. ingots 28 mm. in diameter, which were reduced in three passes (with annealings) to 22 mm. Certain of these were also drawn to 20 mm. To be able to compare the properties of alloys of the different compositions, the bars were thoroughly annealed; *i.e.*, annealed to produce the maximum elongation and minimum strength and hardness. To do this the bars were annealed at 950°C., the only variation being in the mode and duration of heating and the rate of cooling. The results are given in Table 18.

TABLE 18.—MECHANICAL PROPERTIES OF ROLLED BRASS

No.	Composition		Rolled	Tensile strength, 1000 lb. per sq. in.		Elastic limit, 1000 lb. per sq. in.	
	Cu	Zn		A	B	A	B
1	99.99	Hot	32.0	33.8	4.6
2	97.66	2.30	Cold	32.4	51.2	3.5
3	94.82	5.14	Cold	34.1	54.0	5.7	52.3
4	89.90	10.09	Cold	36.9	59.7	7.9	56.8
5	85.02	14.93	Cold	36.9	67.6	7.5	61.8
6	79.78	20.14	Cold	41.6	76.2	9.3	71.1
7	75.00	24.88	Cold	43.7	76.8	10.0	75.8
8	71.95	27.98	Cold	44.0	77.5	10.6	72.9
9	70.09	29.88	Cold	44.0	75.8	11.7	73.9
10	67.40	32.54	Cold	42.7	71.2	10.0	68.6
11	64.95	34.99	Cold	43.0	71.1	10.6	69.0
12	62.13	37.83	Hot	51.9	53.4	14.9	16.4
13	60.27	39.68	Hot	53.4	57.9	15.6	17.4
14	57.91	42.00	Hot	56.5	62.2	12.2	17.0
15	55.76	44.20	Hot	47.3	70.3	16.4	15.1

No.	Elongation, per cent.		Brinell hardness		Resistance to impact units	
	A	B	A	B	A	B
1	52.5	48-49	48-50	18.7	18.7
2	58.0	10.5	48-50	94	19.3	21.2-22.5
3	57.5	11.0	52	99-101	20	23.5-26.2
4	54.0	9.0	55-58	113-116	20.6-21.2	22.5-23.7
5	58.0	10.5	57-58	136-137	23.7-25	14 -14.5
6	72.0	9.5	60-63	156-159	22.5-23.7	12 -13.0
7	77.0	10.0	60-62	164	22.5	12
8	77.5	10.0	70-61	159-168	22.5	9.5-10.5
9	73.5	9.5	60-64	158-161	21.8	9.0-10.5
10	72.5	9.5	56-60	157	20.6-21.2	9 -11.5
11	73.0	10.0	62	146-149	21.2-22.5	9.3-11.2
12	57.0	57.5	80-81	82	20.0-21.8	15
13	50.0	46.0	81-82	94-95	22.5-20.5	13
14	51.0	45.0	92-95	105-107	18.1-20.6	11.5-13.0
15	40.0	35.5	121-131	124-134	16.8-24.3	12.0-14

A = Annealed.

B = As rolled.

Resistance to Impact—Italic figures indicate bars fractured.

Tensile bars 13.8 mm. in diameter; gage length = 100 mm.

TABLE 19.—SCLEROSCOPE HARDNESS OF ANNEALED BRASS

No.	Per cent. Cu		
1	100	11-13-15-17-17-12	11-13-16-13-15-17
2	98	11-14-15-15-14-14	12-14-15-11-12-16
3	95	11-13-16-18-15-14	12-14-17-11-13-17
4	90	11-14-17-19-15-14	12-13-18-12-16-17
5	85	11-12-15-19-17-14	12-15-18-11-13-16
6	80	13-17-19-18-14-12	12-14-17-13-17-19
7	75	17-19-20-19-18-16	16-19-17-17-20-17
8	72	15-16-20-20-16-16	15-16-20-14-16-19
9	70	14-17-18-16-14-13	13-14-18-12-13-18
10	67	12-18-18-19-17-19	12-14-19-12-14-19
11	65	14-17-22-20-19-16	14-16-19-15-18-18
12	62	21-20-20-21-21-19	20-20-17-18-18-16
13	60	13-16-19-20-16-12	13-16-17-17-19-20
14	58	15-17-19-19-16-12	13-17-18-18-18-21
15	56	17-19-20-25-24-19	19-22-21-19-22-22

The scleroscope, it was pointed out in particular, failed to give precise results. The results are tabulated in Table 19. The first six figures give the results along one diameter; the second six give the results along a diameter perpendicular to the first.

The impact tests on notched bars showed a considerable degree of toughness for the α brasses, and the $\alpha + \beta$ brasses up to 60 per cent. copper, inasmuch as these bars did not fracture. Bars were also tested before being annealed, for comparison with the annealed bars, to bring out the effect of annealing on ordinary rolled material. These results are given in Table 18. The results of the scleroscope tests of the rolled bars are given in Table 20 which corresponds to Table 19.

TABLE 20.—SCLEROSCOPE HARDNESS OF ROLLED BRASS

No.	Per cent. Cu		
1	100	16-17-17-16-12-11	10-11-12-14-12-11
2	98	20-29-38-33-29-20	24-28-33-33-27-21
3	95	19-30-36-44-38-22	20-35-43-38-29-21
4	90	25-40-45-42-31-28	27-39-47-22-35-40
5	85	22-32-48-44-32-21	27-36-44-47-37-32
6	80	38-43-56-50-42-34	28-42-56-48-32-28
7	75	46-49-57-57-48-29	30-44-56-36-48-56
8	72	29-46-61-48-37-28	35-45-49-44-43-54
9	70	30-43-58-49-38-27	34-48-58-34-56-58
10	67	38-48-53-53-47-38	28-42-54-53-44-27
11	65	29-43-54-52-38-26	42-45-47-36-48-53
12	62	11-17-20-18-13-12	11-16-17-18-14-11
13	60	19-19-21-18-16-11	12-16-19-19-14-11
14	58	15-17-18-18-17-14	18-18-21-17-12-12
15	56	18-23-24-24-20-17	19-23-21-18-22-20

An interesting comparison was made between hot-working and cold-working of two of the alloys. The results are reproduced in Table 21.

These results show that annealing practically removes any differences due to the mode of working of the brasses of the 60/40 class. Guillet also showed that the Brinell hardness is increased somewhat by quenching. The season cracking of these alloys was briefly considered and a composition of 72 per cent. copper was recommended for stampings. Certain features of this work will be considered in greater detail in Part III. Guillet con-

TABLE 21.—AS ROLLED

Comp.	Rolled	Tensile strength	Elastic limit	Elongation, per cent.	Brinell hardness No.	Resistance to impact
60/40	Hot	58.0	17.5	46.0	94-95	13-15
	Cold	81.7	71.1	12.5	179	85-11
62/38	Hot	53.3	16.4	57.5	82	15-16
	Hot	53.9	17.1	51.0	81	17-20
	Cold	75.8	71.1	8.0	164-167	55-65

Annealed at 750° C.						
60/40	Hot	53.5	15.6	50.0	81-82	22.5-25
	Cold	57.5	16.4	54.0	77-79	19.3-20
62/38	Hot	51.9	14.9	57.0	80-81	20 -21.8
	Hot
	Cold	53.3	17.0	52.0	80-81	17.5-18.7

T. S. and E. L. given in 1,000 pounds per square inch.

cluded with Charpy, that the effect of working increases with the ductility and as the elastic limit decreases.¹

Effect of Third Metals.—The effect of third metals on the properties and behavior of brass is of considerable importance, both theoretically and practically, although it will be principally from the practical point of view that the question will be considered here. This entire subject is one which has not received the attention of metallographists which it deserves and which will, undoubtedly, be paid it in the future. At the present writing we are limited to a few empirical facts, based almost entirely upon qualitative results.

The elements which are intentionally added as desirable constituents are tin, lead and iron. These metals may also be undesirable, as well as antimony, arsenic, bismuth, and cadmium, which are always more or less harmful.

Guillet, who has systematically investigated the effect of third metals on brass,² has shown that other metals have somewhat

¹ MATHEWSON and PHILLIPS have continued the work on the working and annealing of brass but their results will not be considered in detail until Part III. *Trans. Amer. Inst. Min. Eng.*, 1916, Vol. 54, p. 608.

² *Comp. Rend.*, 1905, Vol. 140, p. 307; *Rev. de Met.*, 1905, Vol. 2, p. 97; *Comp. Rend.*, 1906, Vol. 142, p. 1047; *Rev. de Met.*, 1906, Vol. 3, p. 159.

the same effect as zinc, only to a greater or lesser degree. He arrived at a formula $A' = A 100 / (100 + q(t - 1))$ in which A is the percentage of copper in the alloy, A' is the apparent percentage as deduced from the microstructure, q is the percentage of the third metal and t is the percentage of the third metal which is equivalent micrographically to 1 per cent. zinc. The values of q found for various metals were: aluminum, 6; silicon, 10; tin, 2; manganese, 0.5; lead, 1; iron 0.9 and cadmium 1. This relationship was found to hold good for a copper content of from 55 to 63 per cent., as long as no new constituent made its appearance on the addition of the third metal. The presence of such a new constituent was found to indicate a marked deterioration in the mechanical properties.

Effect of Lead.—Lead is introduced into brass in the spelter, which should contain below 0.07 per cent. for the best grades of brass. According to Guillet, lead lowers the strength and especially the ductility. It lowers the resistance to impact but does not affect the Brinell hardness appreciably. He found the lead to occur between and surrounding the grains, always in the free state. It is now known that the distribution of lead depends somewhat upon the amount present; thus, if only amounts up to 2 per cent. are present, it remains uniformly distributed, while if 4 per cent. or above is present, it liquates somewhat, particularly if the copper is below 60 per cent. This subject has been studied in detail by Parravano, Mazzetti and Moretti.¹ They found, as Carpenter did,² that lead exerts no influence on the thermal critical points of brass, and concluded that lead remains undissolved.

If brass of high ductility is desired for technical operations, the lead should be below 0.10 per cent. For this reason only the best grade of spelter is used in the manufacture of brass for cartridges.

The effect of lead on the properties of brass, and its addition to secure suitable machining properties, is very important in certain industries. Sperry³ noted the decrease in tensile strength and ductility by the addition of lead but held that this did not account for the easier machining, which, on the other hand, must be due to lack of cohesion between the grains, as compared with

¹ *Gazz. Chim. Ital.*, 1915, Vol. 44, II, p. 475.

² *Journ. Inst. Metals*, 1912, No. 2, p. 51.

³ *Trans. Amer. Inst. Min. Eng.*, 1897, Vol. 27, p. 485.

brass free from lead. He gave as precautions necessary in the manufacture of screw, rod, or clock brass: Copper should be between 60 and 70 per cent., the lead 2.00 per cent. ± 0.25 per cent., and tin should be under 0.10 per cent. The material should be cold worked as much as possible. The tensile strength should lie between 50,000 and 70,000 pounds per square inch and the elongation between 5 per cent. and 25 per cent. in eight inches. The usual composition is copper 60 per cent., zinc 38 per cent. and lead 2 per cent.

Effect of Tin.—Tin, in small amounts, is seldom harmful, except in lead-brass which it hardens too much for easy machining. "Naval brass" contains about 1 per cent. tin (composition is Cu 67 per cent., Zn 32 per cent., and Sn 1 per cent.) on account of the greater resistance to the corrosive action of sea water. The properties of the ternary alloys of copper, tin and zinc have been determined by Thurston,¹ who found, first the increase in strength and then the great drop in ductility on increasing the tin over 2 per cent. "Spring brass" is made with tin as a stiffener.

The structural changes accompanying this change in properties have been studied by Guillet² and by the writer³ and in considerable detail by Hudson and Jones.⁴ The latter authors, who consider the change at 460°C. to be represented by $\beta = \beta'$, summarized their work by a diagram giving the amounts of tin which dissolve in the α and β constituents. Their work agrees very well with what is known about the effect of tin on the mechanical properties of brass.

The effect of tin and lead on brass has been considered by Johnson⁵ whose work verifies that of others in this field. Particular attention was called to the necessity of annealing brass containing tin at temperatures above the eutectoid point, the eutectoid being the same as the one in the copper-tin alloys. By annealing, the tin is absorbed and the formation of the brittle constituent is prevented. No relation was found to exist between the tin and the lead. Charpy pointed out in 1893 that 0.2

¹ "Materials of Engineering," Part III; "Brasses and Bronzes."

² *Loc. cit.*

³ *Journ. Inst. Metals*, 1913, No. 2, p. 235; also 1915, No. 2, p. 182.

⁴ *Ibid.*, 1915, No. 2, p. 98.

⁵ *Journ. Inst. Met.*, 1912, No. 1, p. 201; also 1914, No. 2, p. 111.

per cent. lead and tin lowered the temperature at which zinc is burnt out of brass from 800°C. to 400°C.

Effect of Iron.—Iron, like tin, can be added to brass in small quantities without materially altering the microstructure but with a considerable effect on the properties. Generally from one to two per cent. is added to brass containing about 40 to 45 per cent. zinc. It increases the strength, hardness, and toughness of brass, without destroying its ability to be worked, either hot or cold. The effect of iron has not been investigated in the same manner that the effect of tin has, but it is fairly well known that iron in excess forms a brittle compound with zinc. The influence of iron up to 1.60 per cent. on the strength of brass with 60 per cent. copper was found by Guillet to be very small.

The best known of the iron-brasses is Delta Metal, which contains about 55 per cent. copper, 43.5 per cent. zinc, 1 per cent. iron and small amounts of lead, manganese, aluminum, and tin. Two other alloys of this class are Aich's Metal and Sterro Metal with 60 per cent. copper, 38 per cent. zinc, and 1.5 per cent. to 2 per cent. iron. The tensile strength of these alloys is about as follows, according to Law: As cast, 65,000 lbs.; as forged, 76,000 lbs.; and as cold drawn, 85,000 lbs. The elongation on eight inches runs as high as 39 per cent. for annealed material.

The principal advantages of the iron-brasses are great strength and toughness combined with fair ductility and a superior resistance to corrosion, as compared to ordinary brass. Delta Metal is also said to retain its strength at elevated temperatures more satisfactorily than does brass without iron.

Effect of Antimony.—Antimony is known to have a bad effect on brass so that the copper, spelter, and scrap used should be free from it. According to Sperry,¹ antimony affects brass like phosphorus affects steel, and produces cold-shortness and coarse crystallization. According to the data given by Sperry, 0.02 per cent. antimony can be detected with certainty and the best brass should contain below 0.01 per cent. antimony. This antimony, when present, is introduced in the electrolytic copper used. Vickers has reported that antimony has a decidedly harmful effect in all brass mixtures, even though they are of low grade.²

¹ *Trans. Amer. Inst. Min. Eng.*, 1898, Vol. 28, p. 176.

² *Foundry*, 1913, Vol. 41, p. 322.

Effect of Arsenic.—Arsenic has the same effect as antimony in producing brittleness in brass, but it also increases the fluidity and improves the casting properties.¹ As little as 0.5 per cent. produces coarse crystallization in 60:40 brass. Smaller amounts, down to 0.02 per cent., have the same effect only to a lesser extent. This amount of arsenic is enough to break up the copper oxide and to produce a clean and fluid material with exceptionally high ductility. With 0.01 per cent. the results are not so good. Arsenic has about the same effect on α brass and, in small amounts, appears to be beneficial. Arsenic in amounts up to 0.1 per cent. in cast brass, or 0.2 per cent. in annealed brass, remains in solution in the α . If more than 0.5 per cent. arsenic is present, the arsenide forms as a brittle intergranular cement.²

Effect of Bismuth.—Bismuth separates out between the grains on solidification and produces brittleness in brass, much the same as it does in copper.³ For this reason, according to Sperry, it should be kept below 0.02 per cent. in 60:40 brass and below 0.01 per cent. in 70:30 brass.⁴ The effect of bismuth is not as marked as that of antimony and most commercial copper is sufficiently free from it for commercial purposes.

Effect of Cadmium.—Guillet reported that cadmium behaves similarly to lead and should be kept low. According to Sperry, the effect of cadmium on brass, in amounts likely to be introduced in ordinary zinc, is practically nil. The ductility and rolling properties of a 60:40 brass were not materially affected by as much as 1 per cent. cadmium. Present opinion seems to be that the amounts of cadmium ordinarily present in brass are not harmful.

This opinion is fortified by recent work of Guillet who showed that 1 per cent. in the 60:40 brass and even greater amounts in the 70:30 brass are not harmful. Cadmium up to 1 per cent. is dissolved in the brass; between 1 and 2 per cent. it forms thin films; and, above 2 per cent. it forms globules.⁵

Of the common metals which are added to brasses of the 60:40 type as strengtheners, we may say aluminum is the most effective, after which come tin, manganese and iron. The effect is

¹ SPERRY, *Brass World*, May, 1906, p. 163.

² See SMALLEY, *Journ. Soc. Chem. Ind.*, 1917, Vol. 36, p. 429.

³ See STEAD, *Journ. Soc. Chem. Ind.*, 1897, Vol. 16, p. 208.

⁴ *Trans. Amer. Inst. Min. Eng.*, 1898, Vol. 28, p. 427.

⁵ GUILLET, *Rev. de Met.*, 1919, Vol. 16, p. 405.

more pronounced on the yield point and elongation than on the tensile strength. This applies particularly to sand castings.¹

Industrial Uses.—The brasses may be very conveniently divided into "cast brass," "low brass," and "high brass," following the classification adopted by Law.²

Brass used for casting purposes may be subdivided into "tombac" and similar alloys, and ordinary brass. "Tombac" (also known as Mannheim gold, pinchbeck, French orfide, etc.) contains from 10 to 20 per cent. zinc and is used principally for ornamental purposes on account of its golden color, which particularly resembles gold when it contains about 10 per cent. zinc. This alloy can also be stamped and otherwise worked cold.

Ordinary brass castings are made with a considerable variation in composition and degree of purity. The metal must be fluid and capable of taking a high polish. A very common mixture is 66 per cent. copper and 32 to 34 per cent. zinc with small amounts of tin, lead and iron as impurities. Considerable scrap is allowable in its manufacture.

Low brass contains from 55 to 63 per cent. copper and is used for extruding and hot rolling. The commonest of these mixtures is one with 60 per cent. copper and 40 per cent. zinc, known as Muntz metal, which is rolled into sheets, shapes, etc. The ductility of brass of this composition when cold is very low, so that all work is done at high temperatures at which the alloys are homogeneous β . The addition of small amounts of iron improves the ductility and resistance to corrosion.

High brasses contain more than 60 per cent. copper and have sufficient ductility to permit their being worked cold. The 70:30 mixture is very commonly used in the manufacture of tubes and wire. This is the alloy with the maximum elongation, and it possesses a fair strength. On account of the ease with which this alloy can be worked cold, considerable of it is used in the wrought condition. This cold work hardens the material so that it must be repeatedly annealed to remove the internal strains which would otherwise lead to distortion of the finished section or even to "season cracking." Boiler tubes and condenser tubes are made of this alloy.

¹ MILLINGTON, *Journ. Soc. Chem. Ind.*, 1918, Vol. 37, p. 149.

² For more complete details on the manufacture and uses of brass, see LAW, "Alloys," SEXTON, "Alloys," BRANNT, "Metallic Alloys," The Mechanical Engineers Handbook, LEDEBUR, "Die Legierungen," FERMUM, "Legierungen," GUILLET, "Alliages Metalliques."

THE BRONZES

Copper-Tin Alloys.—The copper-tin alloys, on account of their great technical importance, early received the attention of metallographists,¹ and a fairly definite understanding of their constitution was given in 1903 by Heycock and Neville in their now classical paper.² Their work was checked and amplified by Shepherd and Blough in 1906,³ who may be said to have given us the constitution diagram in its present form. Their diagram has accordingly been used as the basis of the diagram in Fig. 49. A further confirmation of the constitution diagram is to be had in the work of Giolitti and Tavanti in 1909.⁴

The Constitution Diagram.—The maximum amount of tin which copper is capable of retaining in solid solution was determined by Shepherd and Blough to be 13 per cent. Generally, copper retains a smaller amount, due to a more rapid rate of cooling, and this may be as low as 5 per cent., according to Giolitti and Tavanti. The limit of saturation may be said to be around 9 per cent. in the ordinary case. If there is any tin in excess of this amount, the peritectic reaction is passed through with the formation of β , a solid solution, which at a lower temperature breaks down into the eutectoid of the α and δ constituents. The temperature of the eutectoid inversion has been given as 500°C. but 525°C. seems to be a better figure and has been used in the diagram. The present writer was able to show that there exists another, although small, heat effect at 600°C. which evidently accompanies a reaction between α and β . This is indicated by the dotted line.

The appearance of the α solid solution (dendrites) and the $\alpha + \delta$ eutectoid is shown in Fig. 50.

The constitution of the alloys on the tin side of the eutectoid

¹ The microscopical examination was taken up in 1893 by BEHRENS and described in his work, "Das mikroskopische Gefüge der Metalle und Legierungen," 1894, while the freezing point curves of the Cu-Sn system appeared for the first time in 1895, in the *Bull. d. l. Soc. d'Enc.*, p. 573, as determined by LE CHATELIER, and in the 4th Report to the Alloys Research Committee, 1897. CAMPBELL, in an Appendix to the 5th Report, 1901, reported on his investigation of the microstructure of these alloys as an attempt to explain the freezing point curve and the thermal critical points.

² *Phil. Trans.*, 1903, Vol. 202, p. 1.

³ *Journ. Phys. Chem.*, 1906, Vol. 6, p. 515.

⁴ *Gazz. Chim. Ital.*, 1909, Vol. 38, p. 209.

(above 26 per cent.) is given here as determined by Shepherd and Blough, with the exception that the alloy corresponding to Cu_3Sn is shown to have a freezing point, instead of a range of solidification. This corresponds to the diagram of Giolitti and Tavanti and has been checked in the writer's laboratory. The δ constituent was found by Shepherd and Blough to have a range of stability of several per cent. and to be stable, when free, up to 600°C .

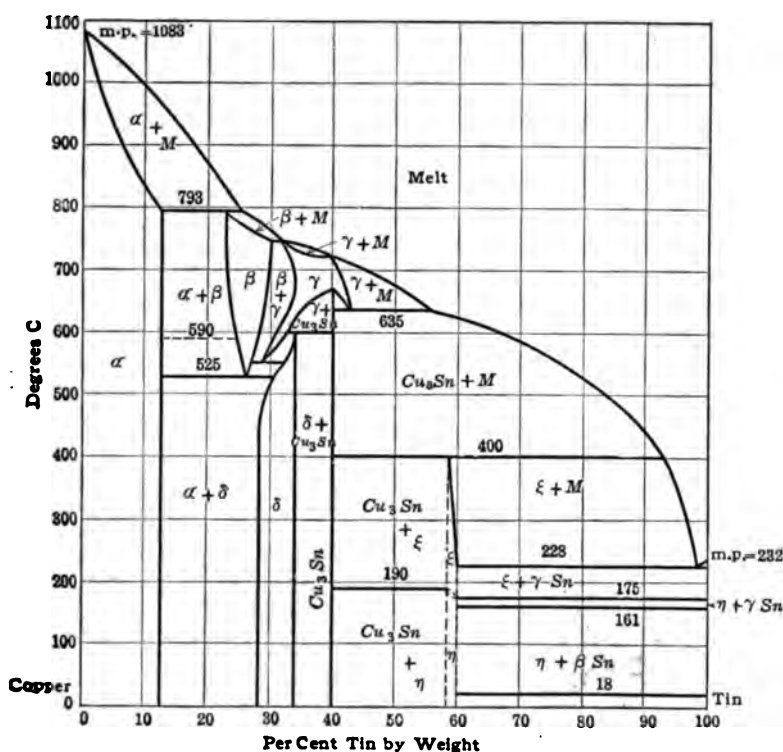


FIG. 49.—The copper-tin constitution diagram.

By quenching alloys of the $\alpha + \delta$ type, the β constituent may be retained, as shown in Fig. 51. Microscopically, there is very little difference between β and γ , and Heycock and Neville, while recognizing that the peritectic horizontal at 740°C . necessitated two phases in this region, were unable to indicate the boundaries of the fields. Shepherd and Blough drew in the $\beta + \gamma$ field, as well as the $\gamma + \delta$ and $\beta + \delta$ fields, from micro-

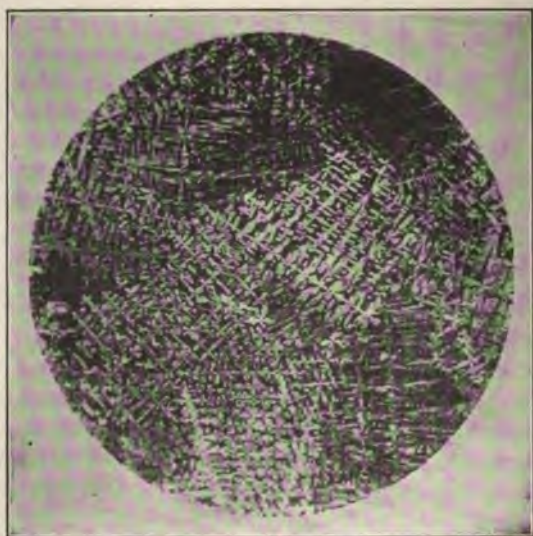


FIG. 50a.—Dendritic structure in bronze, furnace cooled.
Etched with $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$.

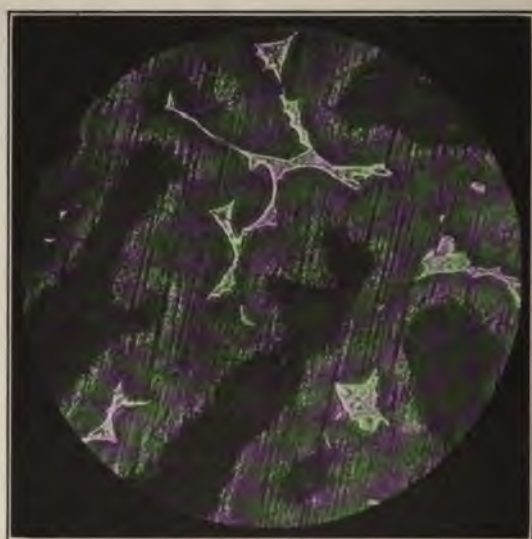


FIG. 50b.—Same as a, showing $\alpha + \delta$ eutectoid. (Rawdon,
Bureau of Standards.)

graphical evidence. In view of their failure to present their evidence and the (theoretical) errors in the construction of the diagram (errors of the same order of magnitude as parts of their fields) it will be necessary to await the results of further research before these fields can be drawn in with certainty.

The constituent δ was shown to be a solid solution and not a compound Cu_3Sn , as had been supposed up to their time. The shape of their δ field may also have to be changed, as further work is done, although the micrographical evidence seemed to be quite clear.

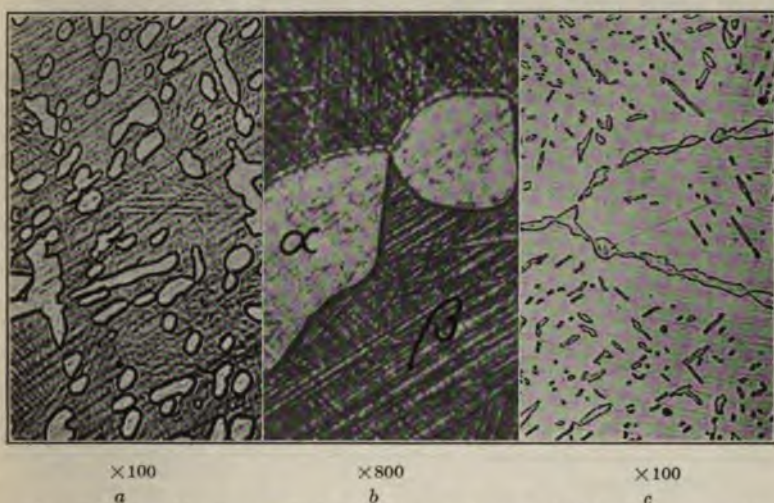


FIG. 51.—*a* and *b*—bronze with 21 per cent. tin, quenched from above 600°C .; structure is $\alpha + \beta$, the latter exhibiting a characteristic acicular structure. Ferric chloride etch. *c*—bronze with 25 per cent. tin, quenched from 550°C . Cupric chloride etch showing α segregate in β .

The compound Cu_3Sn is now known to be an intermetallic compound from both the microstructure and the physical properties, which check each other very satisfactorily. The location of the solidus in this region by Heycock and Neville was accepted by Shepherd and Blough. Giolitti and Tavanti introduced a modification of the Shepherd-Blough diagram, as they represented γ of this composition as melting at a constant temperature, which indicates that Cu_3Sn does not pass through the transformation $\gamma \rightleftharpoons \text{Cu}_3\text{Sn}$ before melting, but that the change is more likely from one kind of Cu_3Sn to another, such as $\beta \text{ Cu}_3\text{Sn} \rightleftharpoons \alpha \text{ Cu}_3\text{Sn}$. The β , or high temperature modification, is capable

of dissolving both copper and tin in solid solution. This interpretation is in complete agreement with the work of Bornemann and Wagenmann¹ on the electrical conductivity of the copper-tin alloys in the liquid state,² according to which the compound must exist at temperatures just above the liquidus.

One remarkable occurrence is the partial fusion of the alloys containing between 38 and 41 per cent. tin after complete solidification has taken place. This results from the reaction $\gamma \rightleftharpoons \text{Cu}_3\text{Sn} + \text{Melt}$, as was first shown by Heycock and Neville.

The ϵ constituent has been dealt with in detail by Houghton,³ from whose work that part of the diagram in Fig. 48 has been constructed. This part as well as the tin side of the diagram is of lesser interest here and will not be considered.

Physical Properties.—The determinations of the physical properties of the copper-tin alloys, it may be said, have verified the constitution diagram. Of this work, the most important are the determinations of the electrolytic potential,⁴ and electrical conductivity,⁵ both of which clearly bring out the δ and the Cu_3Sn constituents. These methods, while yielding positive results, are much less advantageous for studying the α and $\alpha + \delta$ alloys, than the thermal and microscopical methods. The electrical conductivity, as determined by Matthiessen, is given in Table 22.

TABLE 22—RELATIVE ELECTRICAL CONDUCTIVITIES OF THE BRONZES

Copper, per cent.	Tin, per cent.	Electrical conductivity, Ag = 100
100	93.16
98.59	1.41	62.46
93.98	6.02	19.68
88.39	11.61	12.10
87.65	12.35	10.15
85.09	19.41	8.82

¹ *Ferrum*, 1913-14, Vol. 11, p. 276.

² See also RUER, *Zeit. phys. Chem.*, 1907, Vol. 59, p. 1, and 1908, Vol. 65, p. 357; also SIEVERTS, *Zeit. Elektrochem.*, 1910, Vol. 16, p. 707.

³ *Journ. Inst. Metals*, 1915, No. 1, p. 222.

⁴ See LAURIE, *Journ. Chem. Soc.*, 1888, Vol. 53, p. 104; PUSCHIN, *Zeit. anorg. Chem.*, 1907, Vol. 56, p. 1; SACKER and PICK, *Zeit. anorg. Chem.*, 1908, Vol. 58, p. 46.

⁵ See GUERTLER, *Zeit. anorg. Chem.*, 1906, Vol. 51, p. 397. LEDOUX, *Compt. Rend.*, 1912, Vol. 155, p. 35; PUSCHIN, *Journ. Russ. Phys. Chem. Soc.*, 1913, Vol. 45, p. 746.

The specific volume-concentration curve is somewhat irregular towards the copper end but it clearly indicates the compound Cu_3Sn , which has a considerably smaller specific volume than the mean of the components.¹ The volume changes on solidification and further cooling were determined by Houghton and Turner² who showed that as the solidification interval increases, the expansion on solidifying also increases. The maximum at 30 per cent., which could not be readily accounted for, was the only exception. The volume changes at the eutectoid point, while recorded on the curves, were of a much lesser magnitude. It was suggested that the coefficient of expansion of pure β is greater than that of either α or γ , while that of $\alpha + \beta$ is smaller than that of $\alpha + \delta$. It was pointed out by Desch, in the discussion, that it could not be assumed from the curves that the specific volume of the alloys actually increases on solidification, but that the apparent expansion of the bars must be explained on other grounds.

The scleroscopic hardness of the series was determined by the same authors and was found to increase very slowly to a value of about 8 at 11 per cent. tin, and then to rise rapidly to 100 at 28 per cent. tin, which was the hardest member of the series. The hardness of pure tin was 5. The authors found it disconcerting to find that "the scleroscope returns gun-metal as only slightly harder than tin."

The Mechanical Properties of Bronze.—A very complete report on the properties of the copper-tin alloys as determined by the United States Board and others is given by Thurston in his "Materials of Engineering," Vol. III.³ This work shows that tin increases the tensile strength from about 25,000 pounds for pure copper to about 40,000 pounds at 19 per cent. tin.

The properties of the copper-tin series as determined by Shepherd and Upton, who used a method of casting the test bars which gave the maximum results, although not necessarily "fancy," were somewhat higher. The maximum fell again at 19 per cent. tin, the bar, as cast, having a tensile strength of 54,000 pounds and an elongation of 2.9 per cent. on three inches (diameter of test bar = 0.42"). Fracture in all the bars occurred without

¹ MAEY, *Zeit. phys. Chem.*, 1901, Vol. 38, p. 289.

² *Journ. Inst. Metals*, 1911, No. 2, p. 192.

³ See also LAW, "Alloys." This report is given in full in "Tests of Metals," the Watertown Arsenal, 1881, Vol. 1.

the necking customary with steel, so the elongation is practically independent of the gage length.

The alloy with 90 per cent. copper had the following properties:

TABLE 23.—MECHANICAL PROPERTIES OF BRONZE WITH 90 PER CENT. CU AND 10 PER CENT. SN

Condition	Tensile strength, lb. per sq. in.	Elongation, per cent.
As cast.....	44,000	15
540°C. one week, aqua.....	45,000	38
400°C. one week, furnace cooled.....	40,000	25
Heated to red, aqua.....	44,500	21

Aqua = quenched from temperature in water. Results are average of "good" bars.

The authors remarked in their summary (1) that heat treatment has but slight influence on the properties; (2) bronzes with 74 to 87 per cent. copper are stronger if annealed above the eutectoid point than below; (3) prolonged annealing lowers the strength but increases the ductility; (4) quenching from a red heat increases the ductility of bronze and, if the copper content is below 88 per cent., also increases the strength.

The mechanical properties of ordinary cast bronze containing up to 21 per cent. tin are given by Guillet.¹ These are reproduced in Table 24. Variations from these results of several thousand pounds may be expected.

TABLE 24.—MECHANICAL PROPERTIES OF CAST BRONZE

Composition		Tensile strength, lb. per sq. in.	Elastic limit, lb. per sq. in.	Elongation, per cent.	Resistance to impact	Brinell hardness, P = 500 kg.
Cu	Sn					
95	5	27,500	20	9	65
91	9	36,000	14,500	19.5	7	76
89	11	36,500	18,000	16.0	5	88
87	13	36,000	18,500	3	3	95
84	16	35,500	24,000	1.4	0	117
79	21	28,500	28,500	0	0	140

The effect of quenching the $\alpha + \beta$ bronzes from temperatures above the eutectoid point in increasing both the strength and ductility has also been confirmed by Guillet.² The effect of

¹ All. Mét., p. 489.

² See All. Mét., p. 491.

reheating quenched bronzes has been determined by Grenet¹ and Portevin,² but as yet the work is not of practical importance. Goerens and Dumont have determined the effect of annealing (time and temperature) on drawn bronze wire and found that a few minutes at 400°C. removes the effects of cold working.³

Effect of Impurities.—The effect of third metals on bronze has been summed up by Brannet⁴ as follows: Zinc in small amounts (up to 0.5 per cent.) acts as a deoxidizing agent and produces better castings. When the zinc increases over 2 per cent. the strength decreases and a certain brass-like character becomes apparent. Lead is undesirable on account of its liquation, except in certain bearing metals and statuary bronze. Iron behaves somewhat as zinc does, imparting hardness to the alloys, and is sometimes used in machinery bronze. Arsenic, antimony, and sulphur impart brittleness to bronze and should be kept well below 0.10 per cent. Phosphorus acts as a cleansing agent and will be considered under phosphor-bronze. Miller investigated the effects of adding cobalt, zinc, lead, antimony, aluminum, silicon, nickel, tungsten, phosphorus and manganese on copper-tin alloys.⁵ Zinc below 10 per cent. has no appreciable effect on the coefficient of expansion. Cobalt, nickel and manganese cause an increase, antimony and zinc, in excess, a decrease in the strength. The machining properties are improved by 2 per cent. of antimony or lead but not by manganese or nickel.

COMMERCIAL ALLOYS

Coinage Bronzes.—Coinage bronzes contain preferably 5 per cent. tin or, better, 4 per cent. tin and 1 per cent. zinc, the rest being copper. If there is not a great deal of relief in the coin or medal, the tin can be increased up to 8 per cent. Iron is sometimes added (French coins) as a hardener.

Gun Metal.—Gun metal, formerly used in the manufacture of cannon where a strong, ductile and tough material is required, contains about 90 per cent. copper \pm 2 per cent. Generally the remainder is tin but small amounts of zinc, lead and iron are frequently used. Castings which must be strong and resistant to

¹ *Compt. Rend.*, 1911, Vol. 151, p. 870.

² *Compt. Rend.*, 1914, Vol. 158, p. 1174.

³ *Ferrum*, 1913, Vol. 10, p. 21.

⁴ *Loc. cit.*

⁵ *Metallurgie*, 1912, Vol. 9, p. 63.

corrosive action are made of gun metal. The chief difficulty encountered is in eliminating liquation or "tin stains."

The United States Government specifications for gun metal call for a composition of 88 per cent. copper, 10 per cent. tin, and 2 per cent. zinc, with variations under 1 per cent., and iron not to exceed 0.06 per cent. and lead not to exceed 0.2 per cent. It must have a tensile strength of 30,000 pounds, a yield point of 15,000 pounds, and an elongation of 15 per cent. in two inches. This alloy is known as Government Bronze or Admiralty Metal.

The benefits derived from annealing this material, in particular at 700°C., have been determined by Primrose and Primrose.¹ The increase in both strength and ductility, brought about by the absorption of the δ , is shown in Table 25.

TABLE 25.—INFLUENCE OF ANNEALING TEMPERATURE ON DRY-SAND CASTINGS—88-10-2 BRONZE

Mark	Annealing temperature	Time	Tensile strength, lb. per sq. in.	Elongation, per cent.
F.D.N.	38,500	24.0
F.D.A.5	500°C.	30 min.	33,500	26.5
F.D.A.6	600°C.	30 min.	36,500	28.5
F.D.A.7	700°C.	30 min.	40,500	37.5
F.D.A.8	800°C.	30 min.	34,750	31.0

Even more striking results were obtained with chill cast bars as the tensile strength increased to 45,000 pounds and the elongation to 30 per cent. by annealing 30 minutes at 700°C.² The value of annealing castings which must hold water pressure was also brought out. Quenching gun metal seems to be of no value.³

Some very important work on the preparation and micro-structure of standard test specimens has been done at the Bureau

¹ *Journ. Inst. Metals*, 1913, No. 1, p. 158.

² The importance of annealing gun metal has also been shown by SMALLEY who particularly points out the desirability of removing the "cored" structure. *Journ. Soc. Chem. Industry*, 1918, Vol. 37, p. 191.

³ See COMSTOCK, *Foundry*, 1919, Vol. 47, p. 189; and SMART, *Bull. Amer. Inst. Min. Met. Eng.*, 1919, No. 153, p. 1875. It should be noted, however, that large castings are improved by a quenching treatment which inhibits the growth of the α grains and that it is the practice at the Naval Gun Factory, Washington, to quench gun metal castings in water. (McKINNEY.)

of Standards.¹ In this work the best casting temperature was found to lie between 1120°C. and 1270°C. The originals should be referred to for the quantitative results and the effect of mechanical stress on recrystallization.

Effect of Impurities.—Briefly we may say that lead up to 2 per cent. improves the machinability and bearing qualities and does not spoil the alloy for ordinary uses. If the castings are to be used at elevated temperatures, lead should be low. Iron in amounts above 0.3 per cent. makes gun metal brittle. Manganese and silicon are good deoxidizers but the former is more useful in that it improves the strength and toughness. With 10 per cent. tin, not more than 2 per cent. zinc should be added. Aluminum is also beneficial in small amounts as a deoxidizer. Antimony is generally held to be undesirable but gun metal may contain 0.5 or even 1 per cent. without injury. Arsenic is harmful in ordinary sand castings but may actually improve the ductility of small chill castings.²

Statuary Bronze.—There are four important constituents of statuary bronze, as follows: Copper, 88 to 95 per cent.; tin, 2 to 10 per cent.; zinc, 0.5 per cent. to 10 per cent.; and lead, up to 2.5 per cent. Either the tin or the zinc, in any one alloy, should be below 2 per cent. Zinc and lead improve the casting properties and impart a beautiful patina to the statue. A very good account of statuary bronze has been given by Brannt.³

Machinery Bronze and Bearing Metal.⁴—It is well known that certain machinery parts, requiring a moderate degree of strength and ductility, cannot be made out of steel as it corrodes and rusts. Very frequently these parts are made out of bronze, usually one which contains some zinc. Again, as in worm gears, two parts very frequently wear on each other with considerable friction. Of these two, the one which can be more easily replaced is made of bronze so that it may take all of the wear. Table 26 is taken from the reference to give compositions which are commonly used.

¹ See *Technologic Papers*, No. 59, 1916, on the preparation and specifications and microstructure, and No. 60, on the microstructural changes accompanying the annealing of cast bronze.

² See JOHNSON, *Journ. Inst. Met.*, 1918, No. 2, p. 167 and ROLFE, *Ibid.*, p. 263.

³ *Loc. cit.*, page 258.

⁴ See LEDEBUR-BAUER, "Die Legierungen," 1913, p. 125, and a very similar treatise in BRANNT, "Metallic Alloys," 1908, p. 236.

TABLE 28.—MACHINERY BRONZE COMPOSITIONS

Parts	Compositions				
	Cu	Sn	Zn	P	Sb
Eccentric rings.....	84.0	14.0	2.0		
Dense alloy for pump-bodies and valve-boxes.....	88.0	10.0	2.0		
Whistles for locomotives.....	80.0	18.0	2.0		
Same with somewhat duller sound.....	81.0	17.0	2.0		
Stuffing boxes, valve balls.....	86.2	10.2	3.6		
Screw nuts for large threads.....	86.2	11.4	2.4		
Piston rings.....	84.0	3.0	8.5	4.5	
Distributing slide valve.....	82.0	18.0	2.0		
Gears in which teeth are cut.....	88.8	8.5	2.7		
Gears in which teeth are cut.....	87.7	10.5	1.7		
Alloy for mathematical and physical apparatus but slightly subject to changes in temperature.....	82.0	13.0	5.0		
Alloy for more delicate weights, balances, and mathematical instruments.....	90.0	8.0	2.0		
Propeller blades and boxes.....	57.0	14.0	29.0		
Paddle wheel pins.....	76.8	17.4	5.8		
Cog wheels.....	91.0		9.0		
Special high-lead bronze.....	70.0	5.0		25.0	
Lining metal.....				87.0	13.0
Dandelion metal.....		10.0		72.0	18.0
Babbitt, tin-base.....	3.7	88.9			7.4
Babbitt for motor bearings.....	1.0	50.0		38.5	10.5

Copper-Base Bearing Metals.—The conditions which a bearing metal must fulfill (see Chap. II) can be realized with the bronzes, especially those to which lead is added. In this case, however, the relationship between the soft or plastic part and the hard part is generally reversed and we have the plastic lead embedded in a matrix of the bronze dendrites.

The first alloys of this group which were used as bearing metals were the simple or binary bronzes containing about 15 per cent. tin. These alloys consist of crystals of hard δ (as the $\alpha + \delta$ eutectoid) in a matrix of the softer α . This material, while possessing the desirable properties of mechanical strength and low coefficient of friction, lack sufficient plasticity and are too liable to overheat locally. It was soon found that the addition of lead materially increased the plasticity and improved the alloy as a

bearing metal, so that the standard bearing metals of this class contain from 5 to 30 per cent. of lead.

The copper-lead alloys are difficult to cast successfully without liquation. The reason for this is apparent from the constitution diagram. In all cases we have copper forming in a lead-rich melt while if the lead content exceeds about 36 per cent., two liquid layers form. Copper and lead are not soluble in the solid state and the eutectic point is practically the same as pure lead.¹ On account of the liquation of the lead, it was formerly not possible to introduce more than about 15 per cent. lead. Three commonly used alloys contain respectively 10 per cent. tin and 5 per cent. lead, 10 per cent. tin and 10 per cent. lead (S. A. E. specification No. 26 calls for 0.05 to 0.25 per cent. phosphorus), and 8 per cent. tin and 15 per cent. lead (Clamer). The first alloy is used for connecting-rod brasses and the second alloy for bearings (*e.g.*, locomotive bearings) subject to heavy pressure. The latter alloy is the one developed by Dr. Dudley of the Pennsylvania Railroad who found that the wearing qualities were improved by increasing the lead with not too much tin.²

Mechanical properties for alloys of this class are given by Clamer for a one-inch cube as follows.

Alloy			Load at yield point, pounds	Compression of 100,000 lb., per cent.	Relative wear
Cu	Sn	Pb			
85	10	5	24,000	26	
80	10	10	23,000	29	1.00
77	8	15	21,000	..	0.86

Another alloy of this class is the Plastic Bronze of the Ajax Metal Company. This alloy is sold in two different grades, "A" grade containing 5 per cent. tin and 30 per cent. lead, and "B" grade containing 5 per cent. tin and 20 per cent. lead. Grade "A" is intended for general railway work and has a yield point of 16,000 lbs. per sq. in. in compression and a Brinell hardness of 45. Grade "B" is stronger and tougher than grade "A" and is intended for rolling-mill bearings and the like. Its yield point in compression is 19,000 lbs. per sq. in. and Brinell hardness number is 45. Some competitive tests cited by Clamer are reproduced in Table 27.

¹ GIOLITTI and MARANTONIO, *Gazz. Chem. Ital.*, Vol. 40-1, p. 51.

² *Journ. Franklin Inst.*, 1893.

TABLE 27.—COPPER-TIN, AND COPPER-TIN-LEAD SERIES

	Copper	Tin	Lead	Friction	Temperature, ab. room	Wear in grains
1	85.76	14.90	13	50	.2800
2	90.67	9.45	13	51	.1766
3	95.01	4.95	16	52	.0776
4	90.82	4.62	4.82	14	53	.0542
5	85.12	4.64	10.65	18½	56	.0380
6	81.27	5.17	14.14	18½	58	.0327
7	75.?	5.?	20.?	18½	58	.0277
8	68.71	5.24	26.67	18	58	.0204
9	64.34	4.70	31.22	18	64	.0130

COPPER-TIN-LEAD-ZINC SERIES

	Cu	Sn	Pb	Zn	Friction	Temperature, ab. room	Wear in grains
5	85.12	4.64	10.60	18½	56	.0380
10	83.27	5.28	10.25	2.07	18½	68	.0415
11	79.84	4.71	10.30	5.44	18½	66	.0466
12	77.38	5.62	11.42	6.54	18½	68	.0472
13	74.28	4.68	10.61	11.04	18½	69	.0846

Conditions same in all tests

Total no. of revolutions.... 100,000 Journal, 3¾" diam., 3½" long.

Revolutions per minute..... 525 Pressure, lbs. per sq. in. 1000.

Alloy No. 9 is Ajax Plastic Bronze "A." Alloy No. 7 is Ajax Plastic Bronze "B." Lubrication—Galena Coach Oil—Fed by cotton waste.

The tests on the zinc bearing alloys are included to show deterioration caused by the presence of that metal.

Alloys containing 20 to 30 per cent. lead must be handled properly to prevent liquation. This is accomplished by chilling the copper-tin "matrix" and enmeshing the lead in the interstices, from which place it cannot liquate. The addition of a small amount of nickel (1 per cent.) is of great assistance for this purpose. Iron and manganese are also used for the same purpose.^{1,2}

¹ See JONES, *Metal Industry*, April, 1906, p. 81; Anon., *Brass World*, Vol. 6, p. 392 (U. S. P., 971,669); CLARKE, *Foundry*, Vol. 42, p. 219.

² Recently a Cu-Pb bearing metal known as "Kelley Metal" and made by

Alloys of this same type (copper, tin, and zinc) are used for "backings" in car journal bearings, the lining being a lead or tin-base bearing metal, usually tin-base.

Bell Metal.—Bell metal contains more tin than gun-metal, in order to resist the action of the clapper. Ordinarily it contains about 25 per cent. tin for large bells and a smaller amount for smaller bells. Impurities should be kept low. In the manufacture of certain Chinese bells, advantage is taken of the ductility of the β constituent and they are either forged into shape when at a low red heat, or else they are quenched and worked cold.

Speculum Metal.—The alloy with 33 per cent. tin has a pure white color and is capable of taking a very high polish. Accordingly, it has been extensively used in the past for mirrors in telescopes and optical instruments. It is known as speculum metal. Speculum metal has been supplanted by glass mirrors and is of historical interest only.

Manganese Bronze.¹—The term "manganese bronze" is now used for alloys with a considerable variety in composition and properties, although in the majority of cases a brass is meant which has been deoxidized by ferromanganese or pure manganese. Alloys of this type may be divided into two classes, according to Jones,² with compositions as follows:

TABLE 28.—MANGANESE BRONZE COMPOSITION

	No. 1A. For bars	No. 2. For sand castings	Parsons bronze, 1893
Aluminum.....	nil	0.15	0.20
Copper.....	57.35	56.00	56.48
Iron.....	1.40	1.40	1.20
Lead.....	0.03	0.03
Manganese.....	0.02	0.12	0.11
Tin.....	1.20	1.05	1.15
Zinc.....	40.00	41.25	40.84

a special process has appeared. This alloy is said to solidify without liquation and to produce a bearing of exceptional qualities. Its composition is about 67 per cent. Cu and 33 per cent. Pb.

¹ The term "manganese bronze" is a misnomer inasmuch as the alloy is not in any sense a bronze (copper-tin alloy) but is an improved brass.

² *Trans. Am. Inst. Metals*, 1915, Vol. 9, p. 264.

The principal difference is the aluminum which is necessary to secure sound castings in sand molds. These alloys are due to Parsons who first developed the methods for adding manganese to copper alloys on a commercial scale. The composition of one of the early bronzes of this type is added for comparison.

An excellent account of the manufacture of manganese bronze has been given by Sperry.¹ The iron is the principal ingredient affecting the properties of the finished material, the function of the manganese being to assist the copper to take up the iron in solid solution. Lead must be absent so only the best grades of spelter should be employed.

Cast manganese bronze was first used on a large scale in the manufacture of propeller blades on account of its exceptional combination of strength, toughness and resistance to corrosion in sea water. Small amounts of nickel are added to overcome the tendency to erode. It is stated that manganese bronze propellers, due to their freedom from pitting, as compared to an iron one, give an additional speed of about one-half a knot for the same coal consumption (Law). Manganese bronze castings are also used in parts of machinery, pumps, etc., both on account of their great strength (T. S. = 70,000 to 85,000 pounds; Y. P. = 30,000 to 40,000 pounds; elongation in 2 inches = 15 to 30 per cent.) and their resistance to the corrosive action of waters.

Wrought manganese bronze is used, according to Jones, in water supply and irrigation projects, for which purpose forgings over $3\frac{3}{4}$ inches in diameter and more than 25 feet long have been satisfactorily used. It is also used for general forgings for use in mines and in ship construction, and stay bolts, and as extruded parts, such as steam turbine blades. Jones cautions against using expedients to raise the tensile strength above 70,000 pounds, in particular the addition of more aluminum or manganese or the addition of vanadium, titanium, etc., by which means the tensile strength can be raised to 125,000 lbs. but which entails a serious loss in ductility, which drops to at least 20 per cent. Excessive cold work must also be guarded against. He gives as an infallible test for excessive cold work: If the fracture of the test piece is cup-shaped the forging operations have been properly done, but if the fracture is conchoidal and irregular, excessive cold work without proper annealing is indicated. This

¹ *Brass World*, Dec., 1905; see also DEAN, *Metal Industry*, 1911, Vol. 9, p. 4.

is recommended as a test of material which is liable to season cracking.

Pure copper-manganese alloys with 5 to 6 per cent. manganese are also known as manganese bronze. They have been used considerably in continental Europe for stay bolts in boilers as they retain their strength at boiler temperature ($=200^{\circ}\text{C}.$) more satisfactorily than pure copper does.

The following table, taken from Ledebur-Bauer, gives the properties of copper and this type of manganese bronze at elevated temperatures, as determined by Rudeloff.

TABLE 29.—COMPARATIVE STRENGTH OF COPPER AND MANGANESE BRONZE AT ELEVATED TEMPERATURES

Temp., °C.	Copper			Manganese bronze		
	T. S., lb. per sq. in.	Elong., per cent.	R. A., per cent.	T. S., lb. per sq. in.	Elong., per cent.	R. A., per cent.
15	33,700	41.6	67.0	51,000	40.0	72.7
100	29,800	45.2	68.5	50,600	32.4	60.2
200	24,800	44.8	69.0	50,700	36.5	52.4
300	22,300	40.1	52.7	47,600	37.1	51.9
400	13,800	28.4	30.0	36,800	23.7

Tests, carried out under service conditions on the Northern Railway of France,¹ showed a very great superiority for manganese bronze, to such an extent that it is surprising that more attention is not paid to this material. In tests conducted by Hughes² manganese bronze with 7.78 per cent. manganese and 1.82 per cent. iron was shown to have a considerably greater strength, with very good elongation and reduction of area, than the customary grades of arsenical copper.

Aluminum is known to improve the properties of manganese bronze, both the tensile strength and fineness of grain being increased thereby. On account of their fine finish and resistance to corrosion, these alloys are used in the manufacture of parts which come in contact with acid waters. An alloy of this class, known as "Tensilite," has a tensile strength exceeding 100,000 lbs. per sq. in. Its composition has been given as copper 64, zinc 29, tin 0.2, aluminum 3.1, titanium 1.2, manganese 2.5. (Corse and Comstock).

¹ See LAW, "Alloys," p. 124.

² *Journ. Inst. Metals*, 1911, No. 2, p. 74.

Aluminum likewise improves the properties of brass, particularly the 70:30 variety, and produces alloys which are somewhat similar to manganese bronze. Guillet found that the alloy with 70.5 per cent. copper, 26.4 per cent. zinc and 3.1 per cent. aluminum has a tensile strength of 70,500 lbs. per sq. in., an elastic limit of 19,000 lbs., and an elongation of 50 per cent., as compared to 19,600 lbs., 8,000 lbs., and 50 per cent. respectively for the 70 : 30 alloy. Guillet states that the aluminum brasses have the same microstructure as the copper-zinc alloys, except that each per cent. of aluminum has the same effect as $3\frac{1}{2}$ per cent. of zinc.

Vanadium is also added to brass or manganese bronze as a deoxidizer and is said to be very beneficial. Vanadium has the effect of materially improving the quality of the castings, and of increasing the tensile strength and elongation.

Phosphor Bronze.—The beneficial influence of phosphorus on bronze has been recognized for some time, since it was used in France as early as 1854 according to de Ruolz and Fontenay (Ledebur-Bauer). The name is due to Kuenzel who first reported in detail on these bronzes. It is now well known that phosphorus acts as a deoxidizer in copper alloys and that by its cleansing action produces more fluid casts and sounder castings which, compared with ordinary bronzes, possess better physical properties and greater resistance to chemical corrosion. Generally just sufficient phosphorus, as phosphor-copper or phosphor-tin, is added so that, at the most, only traces of phosphorus are left in the final alloy. The probable action of the addition is to reduce the copper oxide with the formation of P_2O_5 , which forms phosphates with basic oxides which may be present. These phosphates are then absorbed by the slag. It is not believed that the addition of phosphorus necessarily reduces all of the oxides which may be present, because if SnO_2 has had a chance to form¹ it is evidently not reduced by phosphorus and the alloy may be then left in a poor condition. The writer has also observed tin oxide in phosphor bronze.

It is also now well known that phosphorus forms a compound with copper, Cu_3P , which in turn forms a (eutectiferous) series of alloys with copper or with bronze.² According to Guillet

¹ See HEYN and BAUER, *Mitt. a. d. kgl. Materialprüfungsamt, Gr. Litch.*, 1904, p. 137.

² HEYN and BAUER, *Metallurgie*, 1906, Vol. 3, p. 73.

the phosphorus first enters the α solid solution of copper and tin and then forms a eutectic, as Cu_3P , with the δ solid solution. If the tin is under about 4.5 per cent., the phosphorus, when greater than 0.3 per cent., occurs as detached particles of Cu_3P , but if there is more than this amount of tin, the ternary eutectic, with 81 per cent. copper, 14.2 per cent. tin and 4.8 per cent. phosphorus, forms.¹ This eutectic melts at 620°C. Copper phosphide is very hard and brittle so that for certain purposes the amount of the phosphorus in the finished alloy should be kept very small. However, as Law points out, alloys containing greater amounts of phosphorus are very valuable for parts which are subject to wear and friction, due to the hard particles of Cu_3P (and the δ solid solution) in a matrix of the strong and plastic α solid solution.

This dual capacity of phosphorus leads readily to a classification of the phosphor bronzes, which is accepted by Law, according to the amount of phosphorus remaining in the bronze. These two classes will now be briefly considered.

It has been stated (Ledebur-Bauer) that by the use of phosphorus, the strength of the bronzes can be increased by 30 per cent. without materially lowering the ductility. This effect is produced by the elimination of the oxides, principally copper oxide. This action is also supposed to account for the greater resistance to corrosion of phosphor-bronze as compared to ordinary bronze. A composition which is used as an acid resisting alloy is copper 90, tin 9.5 and phosphorus 0.5. The following regarding the properties of these bronzes is taken from Law.

"Rolled phosphor-bronze does not suffer any serious loss of strength at temperatures up to 300°C., and it is frequently recommended for firebox plates and stays.

The following table gives some results of tests made upon two well-known brands of rolled phosphor-bronze:

"Samples 1 to 4 are by the Phosphor-Bronze Company, and samples 5 to 7 are "Melloid," by Bull's Metal and Melloid Co.

"Much depends, of course, on the extent of the rolling; but by way of comparison it may be taken that the breaking stress of copper varies from 13 tons (29,000 lb.) per sq. in. in the annealed condition to about 18 tons (40,000 lb.) per sq. in. when rolled.

"As regards the tensile strength of rolled phosphor-bronze at elevated temperatures, experiments carried out on a "Melloid" bolt showed that the breaking stress fell from 28.82 tons (64,500 lb.) per

¹ HUDSON and LAW, *Journ. Inst. Metals*, 1910, No. 1, p. 161.

sq. in. at the normal temperature to 25.51 tons (57,000 lb.) per sq. in. at 315°. On an annealed bolt of the same material the breaking stress fell from 19.22 tons (43,000 lb.) per sq. in. at the normal temperature to 18.80 tons (42,000 lb.) per sq. in. at 215°; while a similar bar of copper, tested under the same conditions, fell from 13.84 tons (28,000 lb.) to 10.25 tons (23,000 lb.) per sq. in."

TABLE 30.—MECHANICAL PROPERTIES OF PHOSPHOR-BRONZE

Sample	Condition	Breaking strength, lb. per sq. in.	Elastic limit, lb. per sq. in.	Elong. per cent. on 2 in.
1	Unannealed sheet.....	63,392	56,000	18.5
2	Unannealed sheet.....	75,712	70,560	17.0
3	Unannealed sheet.....	71,456	71,008	17.5
4	Annealed sheet.....	45,472	17,472	57.0
5	Sheathing plate.....	67,424	18.7
6	Bolt.....	64,512	61,600	26.6
7	Locomotive firebox plate, annealed.....	44,800	64.06

The properties of phosphor-bronze wire have been given by Professor Rogers¹ for an alloy with 95 per cent. copper, 5 per cent. tin, and 0.05 to 0.15 per cent. phosphorus, as follows:

TABLE 31.—PHOSPHOR-BRONZE

Condition	Tensile strength, lb. per sq. in.	Elongation,* per cent.
Spring temper.....	120,000	2
Fine wire.....	160,000	none
Annealed.....	47,000	70

* Gage length not given.

The following mixtures are taken from Ledebur-Bauer.

Parts	Phos. Cu	Cu	Sn	Zn
Steam valves for locomotives.....	3.50	77.85	11.00	7.65
Connecting rod bearings.....	3.50	74.50	11.00	11.00
Railway axle bearings.....	2.50	72.50	8.00	17.00
Railway axle bearings.....	1.50	73.50	6.00	19.00
Piston rods for hydraulic cylinder.....	3.50	83.50	8.00	5.00

The following mixtures for phosphor-bronze have been given by Sperry.²

¹ Metallurgist, Stamford Rolling Mills Company.

² *Brass World*, Vol. 3, p. 399.

Use	Cu, per cent.	Sn, per cent.	5 per cent. phosphor tin, per cent.
Springs	95	4.5	0.5
Bronze of highest strength.....	90	9.0	1.0
Bearing bronze	80	8.0	2.0 (Pb, 10)

Zinc is said to produce liquation and "tin spots."

The bronzes of the second class which are most commonly used contain, according to Law, as follows:

"(1) 8 to 10 per cent. of tin and 0.5 to 0.7 per cent. of phosphorus; (2) 10 to 12 per cent. of tin and 0.7 to 1 per cent. of phosphorus; (3) 10 to 12 per cent. of tin and 1 to 1.5 per cent. of phosphorus.

"The first of these is suitable for valves, pinions, pumps, propellers, steam and boiler fittings, etc. It is harder and wears better than gun-metal. The second alloy is considerably harder than the first, and is suitable for worms and worm wheels, valves, pumps, cylinders, motor gearing, etc. The third is an exceptionally hard alloy without being brittle, and is capable of withstanding the hardest wear. It is suitable for worms and worm gearing, slide valves, bearings, and all cases in which the wear is excessive. For castings the Admiralty specify an alloy containing copper 90.0, tin 9.7, and phosphorus 0.3 per cent. This is required to give an ultimate tensile strength of 17 tons per sq. in., with an elongation of 15 per cent. on 6 in., and to withstand bending over a 2-in. bar until the two sides are parallel without any sign of cracking."

A very excellent contribution on phosphor bronze has been given by Arnold Philip, British Admiralty Chemist, who proposes the following compositions.¹

Use	Cu, per cent.	Sn, per cent.	Phosphorus	Tensile strength, pounds	Elongation, per cent. on 2 in.
Castings of large section.	90.0-92.0	7.4-9.7	0.30-0.60	38,000	<20
Rods, sheet or wire.....	94.5-97.5	Rest	0.10-0.25	67,000	>10(a)
Rods, sheet or wire.....	94.5-97.5	Rest	0.10-0.25	45,000	>40(b)
Bearings.....	1 per cent. or over		

(a) Unannealed; (b) Annealed.

¹ *Journ. Inst. Metals*, 1909, Vol. 1, p. 164.

The excellent mechanical properties and resistance to corrosion would suggest the use of this material as fine suspension but unfortunately, when in thin sections, the elastic properties do not have the required constancy.¹

Aluminum Bronze.—Aluminum added to copper in amount up to about 10 per cent. gives alloys which are very similar to those of copper and tin. Aluminum, like tin, first enters copper

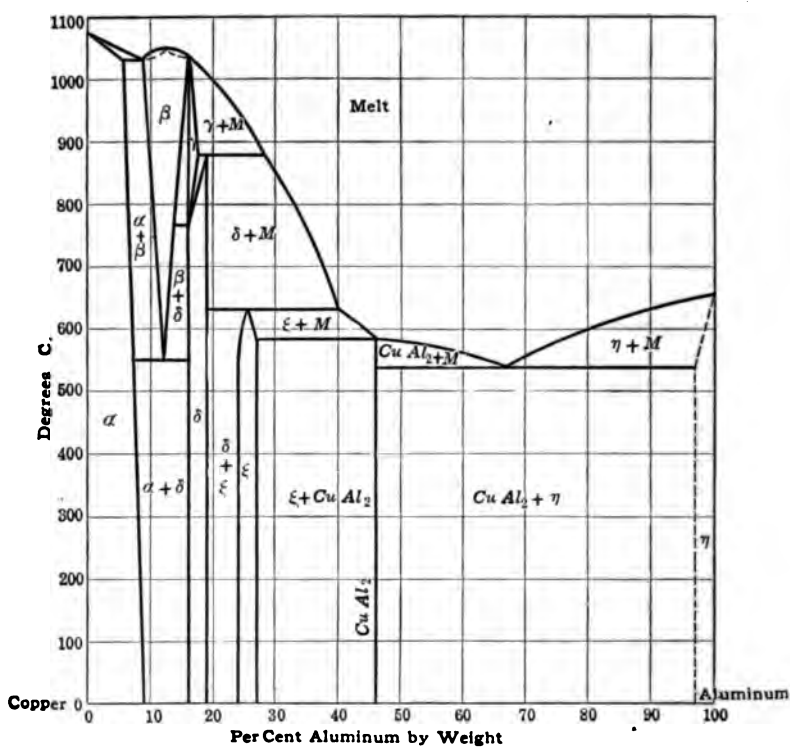


FIG. 52.—The copper-aluminum constitution diagram.

in solid solution and then, when above 7.5 to 8 per cent. forms a second solid solution, known as β , which breaks down into the $\alpha + \delta$ eutectoid at about 550°C. This can be seen from the copper-aluminum constitution diagram in Fig. 52.

The aluminum bronzes possess very valuable technical properties and on that account are exceptionally well suited for a

¹ See PEALING, *Phil. Mag.*, 1915, Vol. 30, p. 203; and OEHLER, *Phys. Rev.*, 1916, Vol. 8, p. 465.

great variety of purposes, but there are certain disadvantages which militate against their general adoption in preference to the ordinary tin bronzes. On this account it will be deemed sufficient here to give only a brief description of the properties and an annotated bibliography for reference.

The advantages of the copper-aluminum alloys are their strength, ductility, resistance to corrosion (not necessarily to tarnishing) and their working properties both hot and cold. As disadvantages which count against their more extended commercial use are their relatively high cost, as compared to brass and bronze, the difficulty in melting and pouring the alloys due to oxidation of the aluminum,¹ and their excessive shrinkage which tends to produce piping and tearing. These alloys are also subject to "season cracking," and the scrap metal is difficult to handle economically.

Properties of Aluminum Bronze.—Certain physical properties of selected alloys, taken from the Eighth Report to the Alloys Research Committee by Carpenter and Edwards, are given in Table 32.

Aluminum bronze is reported to be exceptionally resistant to alternating stresses (White-Souther test), particularly if quenched in water from 850°C. and reheated.² As compared to manganese bronze it appears to be exceptionally resistant and even equals steel in this respect. The tensile properties of these materials were found to be as shown in Table 33.

The manganese bronze contained zinc 41 per cent.; iron 1 per cent.; tin 1 per cent.; manganese 0.5 per cent.; and aluminum 0.5 per cent. The aluminum bronze was a 10 per cent. bronze with 1 per cent. iron.

The manganese bronze failed under a fibre stress of 19,000 pounds per sq. in. at 6,000,000 reversals while the aluminum bronze withstood 13,000,000 reversals at 26,000 pounds per sq. in. as cast, and at least 14,000,000 reversals at 33,000 pounds per sq. in. after quenching and annealing. This exceptional resistance of aluminum bronze corroborates the results secured by Carpenter and Edwards.

¹ The affinity of aluminum for oxygen, which is always present as Cu_2O in commercial copper, is shown by the great amount of heat generated when aluminum is added to copper. This effect was formerly thought to be due to a high heat of formation of these alloys.

² CORSE and COMSTOCK, *Trans. Amer. Soc. Test. Mater.*, 1916, Vol. 16-2, p. 117; see also, *Iron Age*, 1916, Vol. 98-1, p. 80.

ALUMINUM ALLOYS

PROPERTIES OF ALUMINUM BRONZE

Tensile strength, lbs. per sq. in.	Elong., per cent. on 2 in.	R. A., per cent.	Brinell Hd. No.
24.6	46	..	30
40.3	70	..	130
71.6	20	..	215
26.8	40		
40.3	64		
56.0	10		
24.6	40		
44.8	60		
112.0	5		
26.8	46		
44.8	70		
82.8	30		
33.6	58	90	
58.2	83	74	
80.6	30	31	
40.3	42	88	
71.6	48	60	
98.5	12	22	

Tensile strength in 1000 lbs. per sq. in.

TABLE 33

Manganese bronze Aluminum bronze

29,200
87,400
25.0
25.2

20,400
76,900
30.5
27.6

Annotated Bibliography on Aluminum Bronze, Supplementing References in the Text.

I. Constitution.

1905. GUILLET, *Rev. de Met.*, Vol. 2, p. 567.
Results of microscopic and thermal analysis of Copper-Aluminum alloys.
1907. CURRY, *Journ. Phys. Chem.*, Vol. 11, p. 425.
The Cu-Al diagram, as determined by thermal and microscopical examination, is given.
1908. GWYER, *Zeit. anorg. Chem.*, Vol. 57, p. 113.
Structural relations of alloys of Al with Cu, Fe, Ni, Co, Pb and Cd.
1909. GUILLET, *Rev. de Met.*, Vol. 5, p. 413.
Resumé of literature on the Cu-Al alloys.
1913. HANEMANN and MERICA, *Intern. Journ. Met.*, Vol. 4, p. 209.
Critical study of the constitution of the alloys containing from 84 to 90 per cent. copper.
1913. PORTEVIN, *Int. Journ. Metallography*, Vol. 4, p. 257.
A critical study of the β constituent.
1915. ANDREW, *Journ. Inst. Metals*, No. 1, p. 249.
Alloys from 10 to 20 per cent. Al were studied by thermal analysis and the results incorporated into a diagram. The heat effect at 250°C. was explained as being due to partial supercooling of the β solid solution.
1918. GREENWOOD, *Journ. Inst. Metals*, No. 1, p. 55.
A study of the constitution of the copper-rich alloys with particular reference to the hardness as affected by heat treatment.

II. Physical Properties.

1909. PECHEUX, *Comp. Rend.*, Vol. 148, p. 1041.
Study of electrical conductivity and thermoelectric behavior of Cu-Al alloys with 3.5, 6.0, 7.5, 10 and 94 per cent. Al.
1909. BARREÉ, *Comp. Rend.*, Vol. 149, p. 678; *Rev. de Met.*, Vol. 10, p. 16.
A study of the transformation points in aluminum bronze by means of measurements of electrical conductivity.
1912. BRONIEWSKY, *Proc. Int. Assoc. Test. Mater.*, New York. *Comp. Rend.*, Vol. 149, p. 853.
Study of electrical properties of the Cu-Al alloys.
1912. EDWARDS, *Int. Journ. Metallography*, Vol. 3, p. 179.
Study of the hardness of the copper-rich alloys.
1919. ROSENHAIN and HANSON, *Journ. Inst. Met.*, No. 1, p. 260.
The effect of manganese on certain copper-aluminum alloys. The Tomlinson method of "pressure casting" is described.

III. Mechanical Properties.

1907. CURRY and WOODS, *Journ. Phys. Chem.*, Vol. 11, p. 461.
Discussion of methods of melting, casting, and heat treat-

ing the Cu-Al alloys as well as their properties. The constitution diagram, based on heating curves, is also given.

1912. PORTEVIN and ARNOU, *Comp. Rend.*, Vol. 154, p. 511.
The effect of quenching and reheating 10 per cent. aluminum bronze on the tensile properties, hardness and resistance to shock. The accompanying microstructure is also given.
1913. READ, *Journ. Inst. Metals*, No. 2, p. 344.
The effect of phosphorus on certain physical and mechanical properties of a 5 per cent. and a 10 per cent. alloy is given.
1916. PORTEVIN and ARNOU, *Rev. de Met.*, Vol. 12, p. 101.
A further study of the effect of quenching and reheating aluminum bronze.

IV Foundry Practice.

1910. SPERRY, *Brass World*, Vol. 6, p. 3.
Methods of pouring and general characteristics of aluminum bronze are discussed.
1910. CARPENTER and EDWARDS, *Inst. Mech. Eng.*, Vol. 110, p. 701; *Engineering*, Vol. 90, p. 870.
Methods for producing sound castings to withstand hydraulic pressures (14 to 20 tons) are given.
1911. BRASSIERE, *Mech. Eng.*, Vol. 28, p. 712.
Methods of melting and pouring to produce castings free from dross, are given.
1919. CORSE, *Chem. and Met. Eng.*, Vol. 20, p. 162.
Recent experience shows that aluminum bronze can be utilized commercially. See also *Machinery*, Vol. 13, p. 60.
1919. KRYNITZKY, *Chem. and Met. Eng.*, Vol. 21, p. 770.
The use of the 9 per cent. alloy is recommended. Pouring temperature and purity of the materials are important factors. The properties are discussed.

CHAPTER V

STEEL AND CAST IRON

The alloys of iron and carbon, considered from the technical point of view, include the steels and cast irons. These alloys are at once our most important commercial alloys and, besides, belong to one of the most complicated series which has as yet been investigated metallographically. Thus it is that they have been so extensively and intensively investigated and, hence, considerable attention will be given to them here.

THE IRON CARBON CONSTITUTION DIAGRAM¹

The iron-carbon diagram, in a form which except for a few minor details, may be regarded as orthodox, is shown in Fig. 53. This diagram, it should be understood, is not final, but it represents the results of a large amount of work and can be accepted as being sufficiently satisfactory for employment in the metallography of steel and cast iron. From the discussion under Part I, Chapter I, it will be readily noted that the diagram is of Type II, the components of the system being iron and carbon or iron and Fe_3C . In addition, the iron-rich solid solution, on cooling, breaks down into pure iron and Fe_3C according to the eutectoid inversion, γ solid solution $\rightleftharpoons \alpha$ iron + Fe_3C .

The liquidus was determined by Carpenter and Keeling² by thermal analysis, while the temperatures of solidification, or the solidus line, have been determined by quenching experiments by Gutowsky.³ The point E' was located at 1.7 per cent. carbon and 1130°C ., so that all alloys of iron and carbon containing up to 1.7 per cent. carbon solidify as solid solutions of carbon and γ iron.

¹ The present treatise does not aim to be complete but is intended rather to give just sufficient to enable the average reader to understand the technically important points in the metallography of these alloys. A complete discussion of the iron-carbon alloys is to be found in Howe's "Metallography" and GUERTLER's "Metallographie," Part I, No. 2.

² *Journ. Iron and Steel Inst.*, 1904, No. 1, p. 224.

³ *Metallurgie*, 1909, Vol. 6, p. 731.

The two phases, γ solid solution and melt, are both stable and the equilibria between the two are stable so that only one set of conjugate lines is given to represent the field of solid + melt. As will be shown directly, there are two carbon-rich phases—graphite, which is stable, and iron carbide, which is metastable. This has found expression, in certain cases, as a double solidus line instead of the single line just mentioned, one branch representing a carbon solid solution and the other branch representing an iron carbide solid solution.¹ This construction is due, evidently, to the application of the principle of

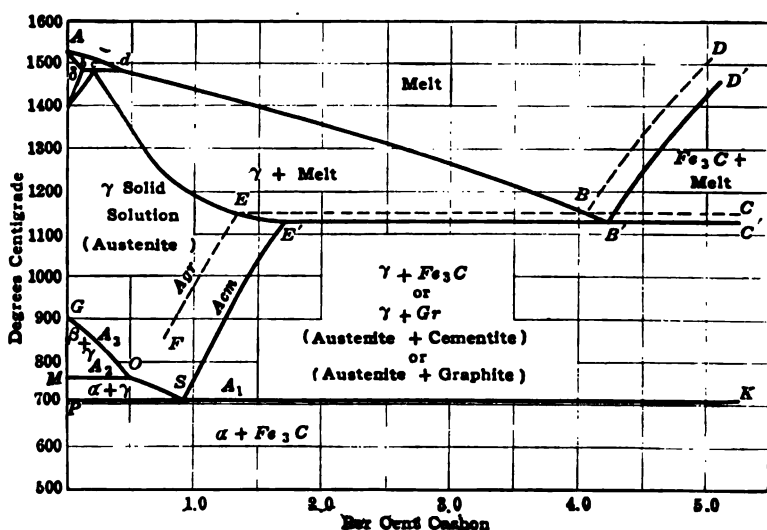


FIG. 53.—The iron-carbon constitution diagram.

the greater solubility of the metastable phase as compared to the stable phase. Inasmuch as the solid solution is a stable phase, the double solidus is not called for, as has been pointed out by Dr. Guertler,² and consequently only a single line, α -E-E' is drawn in Fig. 53. As to the constitution of the γ solid solution, i.e., whether the carbon is in solution as carbon, or as a carbide, let it be stated that the question is quite complex and that it will be referred to at greater length somewhat later on.

It is now generally recognized that there are two carbon-rich

¹ See MARS, *Die Spezialstähle*, p. 58, and UPRON, *Materials of Construction*, p. 139.

² *Metallographie*, Vol. 1, pt. 2.

phases, one of which is metastable but which forms very readily, the carbide of iron- Fe_3C , and the other of which is stable, but which forms rather sluggishly, pure carbon or graphite. This combination of circumstances gives rise to the formation of the carbide in preference to the graphite but also to the more or less immediate change of the carbide into graphite and the iron-rich phase, which may be, according to the temperature, the melt, the saturated solid solution of carbon in γ iron, or α iron. The first, or metastable system, has as its components, iron and Fe_3C , while the second, or stable system, has iron and carbon. On this account it is customary to represent the conditions by means of a double diagram, as has been suggested by Charpy and Heyn.¹ This double diagram is given in Fig. 53, the dotted lines representing the parts of the graphite diagram as closely as is possible at this time.

The Metastable System.—The carbide Fe_3C , containing 6.66 per cent. carbon with a melting point which may be assumed to lie around $2000^\circ\text{C}.$, forms a eutectiferous series with iron, as shown by the solid lines $A-B'$, $B'-D'$ and $E'-C'$ in the diagram. The eutectic point lies at 4.2 per cent. carbon and $1130^\circ\text{C}.$ If the total carbon content is in excess of 1.7 per cent. the composition of the melt will in all cases reach 4.2 per cent. carbon and the freezing of the eutectic will constitute the final step in the solidification. Alloys containing more than 4.2 per cent. carbon, assuming a rate of cooling sufficiently rapid to inhibit the breakdown of the carbide, solidify by separating out primary Fe_3C and then the γ solid solution— Fe_3C eutectic. These latter alloys are of no practical importance,² and need hardly be considered here, although they have been made in the laboratory by very rapidly quenching the melt.³

The Stable System.—It could hardly be said that metallographists agree as to the exact mode of formation of the stable phases in the high carbon alloys, but, in view of what is known of the relative stability and ability to form of the carbide and graphite, the early view supported by Goerens is very acceptable, viz.,

¹ An admirable exposition of the double diagram has been given by BENEDICKS, *Metallurgie*, 1907, Vol. 4, p. 216.

² See HOWE, *Journ. Iron and Steel Inst.*, 1912, Vol. 86, p. 291.

³ See HANEMANN, *Stahl u. Eisen*, 1911, Vol. 31, p. 333, and *Zeit. f. anorg. Chem.*, 1913-14, Vol. 84, p. 1. It was by means of these experiments that the course of the line giving the separation of primary Fe_3C was followed. The graphite line has never been accurately determined.

that graphite is always a decomposition product of cementite.¹ According to this view, alloys containing above 4.2 per cent. carbon would cool below the dotted line, which represents concentrations of the melt which are in equilibrium with graphite, to the solid line, along which the iron carbide separates out. At this temperature iron carbide forms, but, on forming, immediately breaks down into graphite and the melt. This graphite, known as "kish," rises immediately to the surface and escapes. As the cooling proceeds, this operation continues until the melt reaches the eutectic composition. Here solidification is completed by the formation of the eutectic mixture of the saturated γ solid solution and iron carbide, the same as was discussed above. The carbide of the eutectic likewise breaks down, this time into graphite and the saturated γ solid solution. The extent to which this change takes place, in so far as we now know, depends upon two factors—the rate of cooling and the chemical composition, principally the manganese and silicon contents. Slow cooling and silicon promote the formation of graphite while rapid cooling and manganese promote the retention of the carbide.

In the diagram it will be noted that the dotted lines representing equilibria in the stable system lie above the corresponding lines of the metastable system. This is in accordance with a well-known law of physical chemistry which states that the stable phases must always have higher melting or freezing points than the metastable phases. In the present case it has been noted that the alloys melt about 30°C. higher than the temperature of solidification, which must be due to reversion to the stable state.² In other words, melting takes place according to the dotted lines.

Alloys containing well under 4 per cent. carbon (but above 2 per cent.) are seldom met with but their behavior during solidification would be as follows. Along the liquidus, the γ solid solution separates out until the melt reaches the eutectic composition. At this point the carbide eutectic solidifies which may, in turn, form graphite, as was just discussed.

At temperatures below the solidus it will be noted that there are two equilibria—between the carbide and the γ solid solution, and graphite and the γ solid solution. According to the principle that the metastable phase has greater solubility than the

¹ *Metallurgie*, 1906, Vol. 3, p. 175, and 1908, Vol. 5, p. 137.

² See GOERENS, *Metallurgie*, 1906, Vol. 3, p. 181.

stable phase—which might better be stated as “the saturation concentration of the solid solution for the metastable phase is greater than that for the stable phase,”—we would expect two different saturation concentrations at any particular temperature according to whether the equilibrium is between graphite and the γ solid solution or Fe_3C and the γ solid solution.

The solid line, which was determined by Wark, gives the saturation concentrations of the solid solution for the carbide while the dotted line, as determined by Ruer and Iljin gives the saturation concentrations of the solid solution for graphite.¹ Theoretically, graphite would be expected to form as soon as the temperature dropped to the dotted line; as a matter of fact, however, the formation of graphite is very sluggish and the temperature drops to the solid line along which separation of the Fe_3C takes place. The carbide usually persists throughout further cooling so that the alloys behave essentially as represented by the solid lines. We shall see later that γ iron is able to dissolve elementary carbon in amounts as given by the dotted line although the reprecipitation of this carbon is much more difficult to bring about.

These statements might lead to the inference that graphite might be expected to form in steel, especially in steel containing above 1 per cent. carbon. At these comparatively low temperatures graphite does not form unless some exceptional force is exerted tending to make it do so. One such force is due to the presence of a large number of graphite nuclei such as those which form during the malleabilizing of white cast iron. This means that the carbon content must be high, as the tendency for graphite to form increases with the carbon content. Or the presence of considerable silicon may lead to the break down of the carbide even in the steels. The ease with which these graphite nuclei form increases with the temperature so that too high heating may lead to the excessive formation of graphite in tool and cutlery steels. Another force may be that due to internal tensile strains which tend to increase the volume (Mars). Thus it is well known that high carbon steel, if forged at too low a

¹ WARK, *Metallurgie*, 1911, Vol. 8, p. 704. RUER and ILJIN, *Ibid.*, 1911, Vol. 8, p. 97; see also CHARPY, *Compt. Rend.*, 1907, Vol. 145, p. 1277; BENE-DICKS, *Metallurgie*, 1908, Vol. 5, p. 41; HURST, *Engineering*, 1918, Vol. 106, p. 217; MERICA and GUREVITCH, *Technologic Paper*, Bureau of Standards, No. 190-1010

temperature, forms graphite upon being annealed. These internal strains are supposed to arise during forging when the inside is hotter than the outside, which conditions might easily arise if forging is carried to too low a temperature.

The "break down" of the γ solid solution proceeds according to Type IIa with the eutectoid point at 0.9 per cent. carbon, the intersection of the two saturation or segregation lines of the solid solution for iron and the iron carbide. The transformations of a few typical alloys will serve to explain the behavior of this series of steels on cooling.

A low-carbon alloy containing, for instance, 0.2 per cent. carbon, cools to the line G-O before beginning its transformation, whereupon it commences to separate out pure iron in the β , or non-magnetic condition. As the temperature drops further, β iron continues to separate out while the composition of the solid solution shifts along the line G-O-S. At 767°C. the iron which has separated out by this time, becomes magnetic, during which change the temperature remains essentially constant. With further drop in temperature pure iron, now in the α condition, continues to separate out and the composition of the solid solution varies along G-O-S up to 0.9 per cent. carbon at the point S. At this temperature the solid solution becomes saturated with both iron and Fe_3C and thereupon changes over into the eutectoid $\alpha + \text{Fe}_3\text{C}$. During this transformation the system is non-variant and the temperature again remains essentially constant. In an alloy with 0.6 per cent. carbon the temperature drops to the line O-S before the transformation commences. At this temperature magnetic α iron commences to separate out and continues to separate out as the temperature falls until at the line P-S the solid solution, now containing 0.9 carbon, changes over into the $\alpha + \text{Fe}_3\text{C}$ eutectoid.

An alloy with 0.9 per cent. carbon, being of eutectoid composition, cools down to the point S before it undergoes any transformation. At this temperature it becomes saturated with iron and Fe_3C simultaneously and breaks down en masse into the eutectoid.

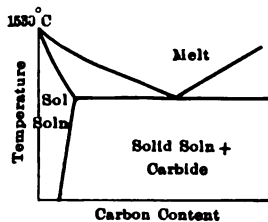
Alloys containing between 0.9 per cent. and 1.7 per cent. carbon behave similarly to those to the left of the eutectoid point except that, of course, the solid solution is of such a composition that it becomes saturated with Fe_3C first. Accordingly, as the temperature falls to the saturation line, Fe_3C commences to

form and continues to form until the temperature reaches the line S-K, whereupon the eutectoid forms as before.¹

For convenience the steels containing less than 0.9 per cent. carbon are called "hypo-eutectoid" steels, those with more carbon "hyper-eutectoid" steels, and those containing 0.9 per cent. carbon, or the eutectoid composition, are called "eutectoid" steels.²

These transformations of the iron-carbon alloys, aside from the magnetic change at A_2 , are due to the A_3 allotropic transformation in iron, accompanied by the drop in solubility of carbon in iron to practically nil, and to the segregation of the iron-carbide from the solid solution.³ At the (accidental) intersection point of the iron and iron-carbide segregate lines, a eutectoid forms in strict accordance with the principles laid down in Part I.

¹ It has been argued that inasmuch as the separation of pure iron involves an allotropic change, $\gamma = \beta$ or α , and that Fe_3C separates out in the same manner, that Fe_3C must be polymorphic, one modification being soluble and the other insoluble in iron. See SAUVÉUR, "The Metallography and Heat Treatment of Iron and Steel," Second Edition, 1916, p. 192. In view of the laws of heterogeneous equilibrium, such a conclusion is neither permissible nor even desirable; in fact, even though iron were not allotropic we could still have a segregation of the carbide from the solid solution, per accompanying diagram, and the grounds for this reasoning would be lacking.



² Professor ARNOLD has suggested the terms "un-saturated," "saturated," and "super-saturated" to denote these different types of steel and they are occasionally employed. That they are not generally used in preference to the terms here given is due to the conflict with the general usage of the term "saturated" as applied to solutions.

³ We find that the practical lack of solubility of carbon in α or β iron is contested from at least one source, the opposing contention being based on the experiment of annealing iron in carbon at a temperature corresponding to its β range, whereupon turnings from the outer layers showed an appreciable carbon content. On examination it is readily seen that this contention is not sound for common salt will liquefy ice at temperatures below $0^\circ C.$ and produce a brine containing salt. This does not prove that salt is soluble in ice, but rather that solid salt and ice can unite to form a solution of salt in water. Consequently this experiment shows merely that carbon and α or β iron can unite to form a solution of carbon in γ iron, a process which is similar to the eutectoid reaction, α iron + $Fe_3C = \gamma$ solid solution, or to the melting of a eutectic mixture.

On heating, these alloys pass through the same transformations in the reverse order, *i.e.*, the α iron and Fe_3C composing the eutectoid dissolve in each other to form the solid solution with 0.9 per cent. carbon with which the remaining α iron (or Fe_3C) is in stable equilibrium. As the temperature is further raised the α iron (or Fe_3C) gradually dissolves in the solid solution. We shall see later that these transformations take place at higher temperatures on heating than on cooling, the difference or "lag" being about 30 to 50°C. The diagram, as usually given, does not bring out this point.¹

STEEL

The term "steel," while it is in very general usage, is one which has no definition which is universally accepted.² It is quite clear that the metallographist can distinguish steel and the cast irons as those alloys of iron and carbon containing up to 1.7 per cent. carbon and above 1.7 per cent. carbon respectively but the historical development has been more influential than the constitution of the alloys in determining the terminology. The high carbon alloys lack malleability and have such low melting points that they have always been cast into shape. Consequently they have been called "cast iron." Carbonless iron, originally made directly from the ore, is malleable and has such a high melting point that formerly it was always wrought into shape. Consequently it was called "wrought iron." There was still another variety or alloy of iron and carbon which could be wrought into shape and which, by suitable heat treat-

¹ Before passing on it should be noted that the condition of the carbon in the melt is of theoretical interest. The most direct method of attack is to calculate the molecular weights of the solute and solvent from the liquidus and solidus lines. One such attempt is that of Cesaro who applied Raoult's law and the LeChatelier-Schroeder formula to the data of Carpenter and Keeling. The conclusion reached was that the iron exists as Fe_2 and the carbon as Fe_3C . While this question at present is purely of scientific interest, it seems quite possible that the condition of homogeneous equilibrium of the melt may have its influence on the properties of the finished steel. A preliminary experiment directed to throw light on this question showed that by highly superheating a melt of hypo-eutectic cast iron, the eutectoid inverted.

² This question has been thoroughly considered by Prof. Howe. See Metallography of Steel

raised. See Metallography of Steel

ment, could be made either soft and malleable or hard and brittle. This material was obviously neither "cast iron" nor "wrought iron" and was termed "steel." This nomenclature was adopted before the chemical nature of iron and steel was understood and before the present steel making processes had been developed. With the introduction of the Bessemer and open-hearth processes, steels of the entire range of carbon content were made. After considerable discussion it was decided to adapt the existing nomenclature to the new products and hence it is that we call the product of the Bessemer or open-hearth processes by the name "steel," regardless of the fact that some of them (those low in carbon) resemble "wrought iron" in properties and some of them (those high in carbon) resemble the original "steel" in properties. Howe has termed this the "industrial" nomenclature and it is generally adopted in this country, Great Britain and France.

There was some objection raised to this nomenclature, particularly in Germany, and so it is that in Germany, Austria and Russia the division between steel and iron is drawn, not according to the process of manufacture, but according to the tensile strength. Thus iron has a tensile strength of less than 5,000 kg. per sq. cm. (71,000 lbs. per sq. in.) when tested in the slowly cooled condition, while steel has a tensile strength of 5,000 kg. per sq. cm. or over. Iron of plastic origin is called wrought iron and iron of liquid origin (cast into ingots) is called ingot iron. The same subdivision is made for steel.

To the metallographist, steel is an alloy of iron and carbon, or, better, iron-carbide, containing usually under 1.7 per cent. carbon, irrespective of the source. In the light of this definition, metallic iron would be called iron (wrought iron, ingot iron, etc.), steel would be the name of an "alloy" of iron with another element, carbon, which would be present in an appreciable amount or at least in sufficient quantities to alter or change the properties of iron. Thus if carbon is intentionally added to iron (or intentionally retained in iron) so as to produce an alloy of iron, the alloy would be called "steel." This distinction between "iron" and "steel" would be much the same as that between copper and bronze. The only confusion in either case would be in determining the amount of carbon (or tin) which fulfills these conditions. It may be of interest to note that the amount of iron-carbide added to iron to change the ~~properties~~

of iron is of the same order of magnitude as the amount of tin added to copper to change the properties of copper.

The principal difficulty in applying the metallographical nomenclature would be, doubtless, in naming the pure iron which is made in the open hearth furnace. The material is iron (99.84 per cent. Fe) and is in ingot form and yet our industrial nomenclature requires us to call it "steel," although in certain places it goes by the name of "ingot iron."¹ In this way the beautiful distinction made possible by metallography between iron, the metal, and steel, the alloy, is lost. This condition will probably be rectified for now that the science of metallography is well founded, and quite universally taught, it will be remarkable if the old and unscientific nomenclatures do not gradually fall into disuse as engineers and others become accustomed to thinking of metals and alloys from the metallographical, or scientific, point of view. In the following, to be logical, steel will be treated as an alloy of iron and iron carbide.

METALLOGRAPHY AND PHYSICAL PROPERTIES OF STEEL

We shall consider here (1) rolled or forged steel, (2) rolled or forged and subsequently heat treated steel, and (3) cast steel. This arrangement appears to be sufficiently consistent for the present discussion and classifies steels according to their commercial uses.

Rolled or Forged Steel.—For the purpose of discussing the microstructure and properties of forged or rolled steel, we may conveniently divide the range up to 1.7 per cent. carbon as follows: low carbon steel containing up to about 0.35 per cent. carbon, medium carbon steels containing from 0.35 to 0.70 per cent. carbon, and high carbon steels containing above 0.70 per cent. carbon. This classification is adopted principally for the purposes of the present discussion although it corresponds, with some degree of accuracy, with the commercial usage.

Low-Carbon Steel.—The steels of this group are characterized, structurally and physically, by pure iron which occurs in polygonal grains as the predominating constituent. Two typical structures of mild steel are shown in Fig. 54. The blank and roughened areas are practically pure iron and are known

rust might better be called "open hearth iron."

as the structural constituent, "ferrite." The dark areas (at X100) are the eutectoid which is composed of alternating platelets of ferrite and the iron carbide, or "cementite." The eutec-

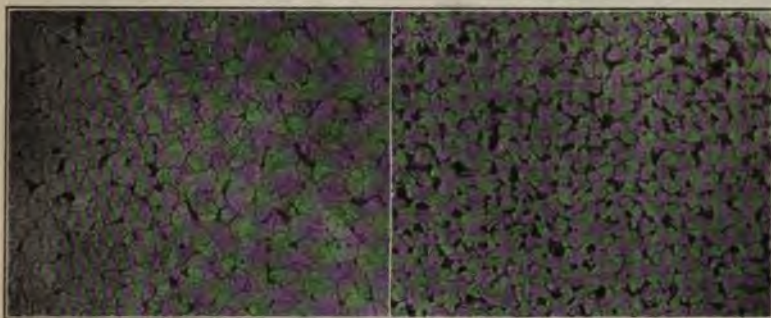


FIG. 54a.

FIG. 54b.

(a) Steel with 0.07 per cent. carbon. (b) Steel with 0.21 per cent. carbon. Ferrite light and pearlite dark. (*Dr. Burgess. Bureau of Standards.*)

toid, which can be seen to better advantage in Fig. 55, is called "pearlite" from its pearly luster on the polished and etched microsection. The polygonal grains of ferrite formed when the steel cooled slowly through the transformation range, and, being



FIG. 55.—Steel containing 0.49 per cent. carbon, annealed at 1100°C. Ferrite and lamellar pearlite. (*Hanemann.*)

so greatly in excess, crystallized much the same as they would in pure iron. The solid solution rests, located probably at or near the centers of the original grains of the solid solution, trans-

formed into the pearlite during the eutectoid reaction and are now located in between the ferrite grains. Ferrite, the predominating constituent, largely determines the properties and behavior of low-carbon steel. The materials classed as low-carbon steel, as well as their common properties, are given in Table 34.

TABLE 34.—PROPERTIES OF LOW-CARBON STEEL

Material	Carbon content	T. S.	Y. P.	Elongation	R. A. per cent
Rivets, wire, tubing, pipe, bars, sheets, cold-worked material, soft forgings. . .	Up to 0.15	45,000–60,000	27,000–36,000	30	60–55
Screw stock, rivets, plates, shapes exposed to shock.	0.15–0.20	60,000–62,000	36,000–38,000	30–26	55–45
Structural steel, plates, reinforcing bars.	0.20–0.25	62,000–72,000	38,000–40,000	26–24	45–40
Stiff structural steel, wire, forgings.	0.25–0.35	72,000–80,000	40,000–48,000	24–22	40–30

T. S. and Y. P. are given in pounds per square inch.
Elongations are given in per cent. on eight inches.

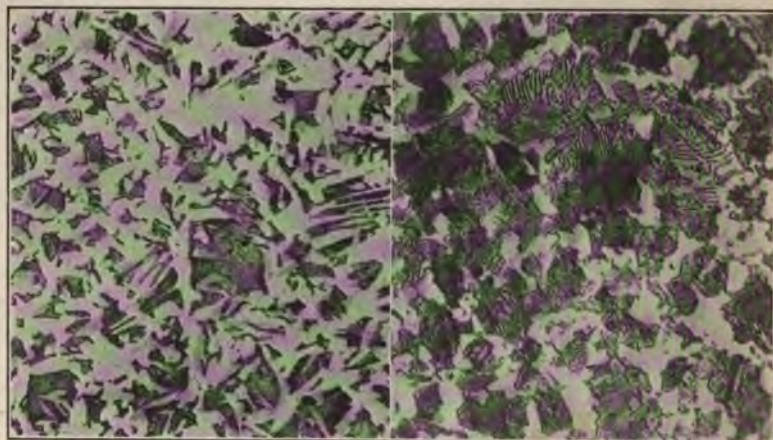


FIG. 56a.

FIG. 56b.

Microstructure of medium-carbon steel. (a) Carbon content Ca 0.30 per cent. (b) Carbon content Ca 0.45 per cent.

These steels, especially those with lower carbon, are useful on account of their weldability and the ease with which they can be worked both hot and cold. The plasticity is shown by the figures for elongation and reduction of area and is a particularly valuable property for wire drawing and stamping or pressing.

Medium-Carbon Steel.—This class of steel contains ferrite and pearlite in more nearly equal amounts but the free ferrite now occurs within and around the pearlite cells. This structure is shown in Fig. 56. The solid solution rests, at the time of their transformation, occupy such a large portion of the steel that the segregated ferrite occurs merely as a net-work

TABLE 35.—PROPERTIES OF MEDIUM-CARBON STEELS

Material	Carbon content per cent.	T. S. lbs. per sq. in.	Y. P. lbs. per sq. in.	Elongation, %	R. A. %
Axles, shafts, piston rods, forgings.....	0.35-0.45	80,000-95,000	48,000-60,000	22-17	30-45
Forgings, axles, shafts, tires.....	0.45-0.60	95,000-113,000	60,000-75,000	16 (2")	30-45
Stiff forgings.....	0.60-0.70	113,000-118,000			

TYPICAL SPECIFICATIONS OF MEDIUM-CARBON STEEL.—(A.S.T.M.)

Material	Y. P., lbs. per sq. in.	T. S., lbs. per sq. in.	Elongation	R. A. %	Remarks
Low-C steel splice bars.....		55-65,000	25% in 8"		C < 0.10%, cold bend 180°.
Medium-C steel splice bars.....		68,000	$\frac{1,600,000}{\text{T.S.}}$		C > 0.30%, cold bend 180°.
High-C steel splice bars.....		85,000	14% in 2"		C > 0.45%, cold bend 90°.
High-C steel splice bars; quenched...	65,000	100,000	10% in 2"		C > 0.60%, cold bend 90°.
C-steel track bolts.	70,000	100,000	12% in 2"		C > 0.30%, cold bend 45°.
Structural steel for bridges.....	0.5 T. S.	55-65,000	$\frac{1,600,000}{\text{T.S.}}$ 8"		Cold bend 180°.
Rivet steel for bridges.....	0.5 T. S.	46-56,000	$\frac{1,600,000}{\text{T.S.}}$ 8"		Cold bend 180°.
C-steel forgings....	0.5 T. S.	75,000	>19.0 in 2"	>24	Untreated. Diam. < 8".
C-steel forgings....	0.5 T. S.	75,000	>20.0 in 2"	>33	Annealed. Diam. < 8".
C-steel forgings....	0.5 T. S.	80,000	>20.0 in 2"	>32	Annealed. Diam. < 8".
C-steel forgings....	55,000(a)	90,000	>20.5 in 2"	>39	Quenched and tempered. Diam. < 4".
Cold-rolled steel axles.....	60,000(a)	70,000	18 in 2"	35	C < 0.40%.
Steel tires:					
Class A.....		105,000	12 in 2"	16	Drop test required.
Class B.....		115,000	10 in 2"	14	Drop test required.
Class C.....		125,000	8 in 2"	12	Drop test required.

(a) Elastic limit by extensometer.

A. For passenger engines.

B. For freight engines, truck and car wheels.

C. For switch engines.

structure. This structural change from polygonal to net-work undoubtedly accounts for the relatively greater decrease in ductility, with increase in carbon content, which occurs at this composition. These steels are of commercial importance on account of their strength, ductility and toughness as well as the ease with which they can be rolled or forged into shape while hot. In Table 35 are given typical medium-carbon steels and their properties.

High-Carbon Steel.—The microstructure of high-carbon steel which has been slowly cooled is characterized by the eutec-

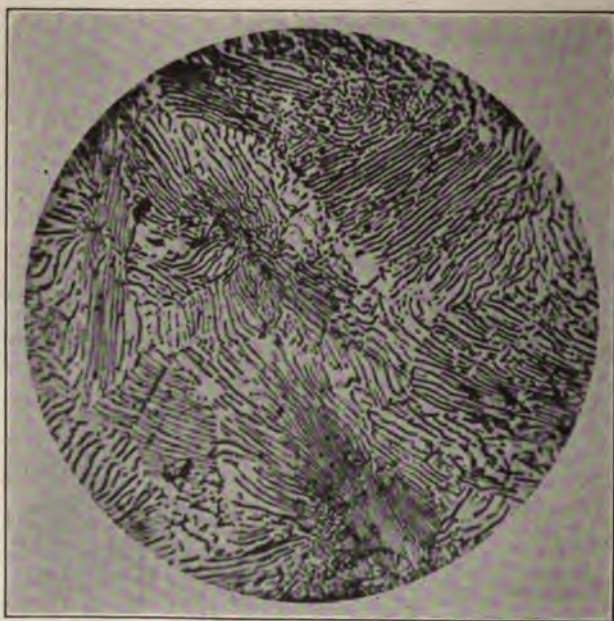


FIG. 57.—Eutectoid steel, lamellar pearlite. (Hanemann.)

toid, pearlite, which can be seen in Fig. 57. Pearlite occurs at times with structurally free ferrite, as in Fig. 56, and again with structurally free cementite, as in Fig. 58. These steels are generally heat treated to bring out the desirable properties and will be considered under heat treatment.

Summary of the Properties of Steel vs. Chemical Composition. Steel, as it is made commercially, always contains small amounts of manganese, silicon, phosphorus, etc. These ele-

ments affect the properties of steel, and formulæ designed to give the strength from the chemical composition take them into consideration. Of all these elements, carbon has the greatest effect on the mechanical properties. This is due first of all to the formation of the compound Fe_3C which contains only 6.7 per cent. carbon, and secondly to the formation, by the carbide, of the eutectoid at 0.9 per cent. carbon. The eutectoid is fine-grained and as is well known, has a decided strengthening effect on steel. If it be assumed that the rate of cooling is such that the eutectoid has ample opportunity to form, the tensile strength

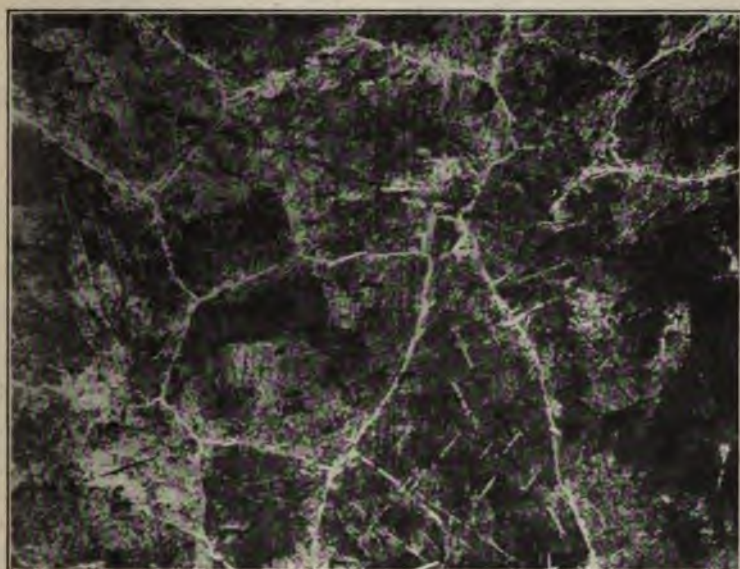


FIG. 58.—Hypereutectoid steel, cementite net-work and pearlite.

then varies directly with the amount of pearlite present, or from 40,000 lbs. for pure iron to 100,000 lbs. at 0.9 per cent. carbon where it reaches a maximum. On the other hand, if the steel is air-cooled, a mild quenching effect takes place in the higher carbon steels and the maximum tensile strength lies at about 1.1 per cent. carbon and 130,000 lbs. This variation in physical properties, as given by Howe, can be seen from Fig. 59.¹

¹ The mechanical properties of steel vs. carbon content have been given by WAHLBERG, *Journ. Iron and Steel Inst.*, 1901, No. 2, p. 29. See also, *Tests of Metals*, The Watertown Arsenal, 1886 and 1887.

Values indicated by the lines in Fig. 59 are average values. Variations from these values would be met with in practice and are due to various causes such as variations in elements other than carbon, the method of manufacture of the steel, the finishing temperature, etc., the more important of which will be considered in the following.

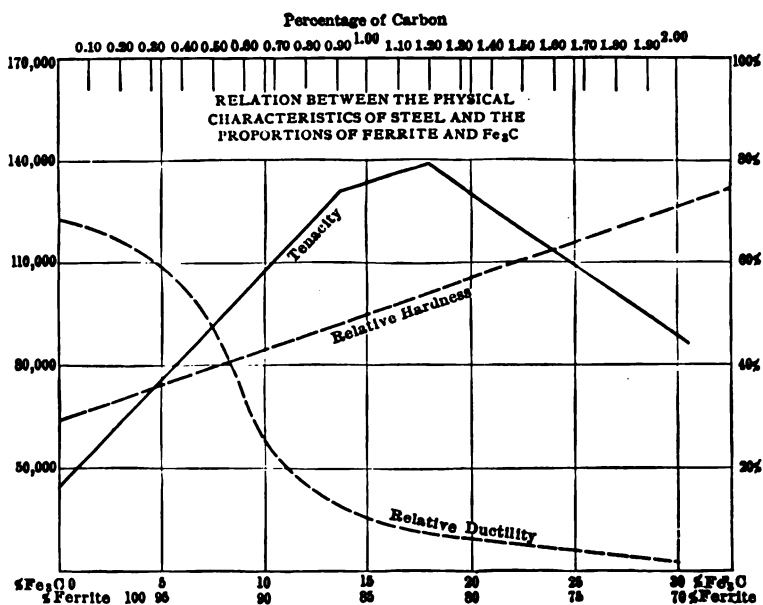


FIG. 59.—From Howe, "Iron, Steel, and other Alloys."

The influence of carbon, manganese, and phosphorus on the properties of steel such as sheets, plates and rolled sections, has been summed up by H. H. Campbell¹ as follows:

TABLE 36

Acid steel.....	T.S. = 40,000 + 1000 C + 1000 P + Mn
Basic steel.....	T.S. = 41,500 + 770 C + 1000 P + Mn

In these formulæ C = 0.01 per cent. carbon determined by combustion, P = 0.01 per cent. phosphorus. The values of Mn are given in the following formulæ:²

¹ The Metallurgy of Iron and Steel, p. 390.

² MERRIMAN has suggested the following forms for these formulæ: For acid steel, T.S. = 40,000 + (680 + 8Mn)C + 1000 P. For basic steel, T.S. = 38,800 + (650 + 4 Mn)C + 1000 P + 90 Mn. *Iron and Steel Magazine*, November, 1905.

Acid steel, $Mn = a(160b)$, where $a = \frac{\text{per cent. Mn} - 0.40}{.02}$

$$\text{and } b = \frac{\text{per cent. C}}{0.10}$$

Basic steel, $Mn = (550 + 100a)b$, where $a = \frac{\text{per cent. C} - 0.05}{0.05}$

$$\text{and } b = \frac{\text{per cent. Mn} - 0.30}{0.05}$$

McWilliam has given the following formula for the tensile strength of basic steel as one-inch round bars which have been given normal treatment.¹

$T.S. = 38,000 + (800 + 4(C - 20))C + 120Si + (100 + 2(C - 20))Mn + 1000P$. In this formula C, Si, Mn and P represent the composition of the steel in these elements expressed in units of 0.01 per cent.

Stead² summarizes the effect of carbon on normalized steel containing less than 0.9 per cent. carbon as follows:

Effect of 0.1 per cent. Carbon

Yield point is raised.....	4,000 lbs. per sq. in.
Tensile strength is raised.....	9,500 lbs. per sq. in.
Elongation is reduced.....	4.33 per cent.
Reduction of area is reduced.....	7.27 per cent.

These figures are averages of the results of Arnold, Brinell, and Harbord, obtained with steel melted in clay pots, and can not be compared with the figures of Campbell.

The tensile strength of steel can be computed on the basis of the relative amounts of the two microconstituents present, ferrite and pearlite. To do this Dalby has proposed the formula

$$f_s = 1.11 C (f_p - f_i) + f_i,$$

where f_s = T.S. of the steel, f_p = T.S. of pearlite or about 139,000 lbs. per sq. in., and f_i = T.S. of ferrite or about 36,000 lbs. per sq. in.³

The method of manufacture has an appreciable effect on the properties of commercial steel as it determines to a large extent the purity of the steel and its solidity, i.e., freedom from slag, gas, and oxides.

The relation between the properties of steel and the process

¹ *Journ. Iron and Steel Inst.*, 1918, No. 2.

² *STEAD, Journ. Iron and Steel Inst.*, 1916, No. 2, p. 5.

³ *Engineering*, 1917, Vol. 103, p. 319.

of manufacture are summed up in the following table, according to Harbord.¹

TABLE 37

Ultimate stress, lb. per sq. in.	Percentage of carbon required			
	Basic O. H.	Acid O. H.	Basic Bes.	Acid Bes.
56,000	0.126	0.110	0.087	
67,200	0.250	0.177	0.170	0.135
78,400	0.360	0.335	0.265	0.246
89,600	0.432	0.407	0.385	0.350
100,800	0.505	0.475	0.461	0.428
112,000	0.585	0.556	0.524	0.495

The Brinell hardness numbers were said to follow the tensile strengths. The reasons for this variation in properties are not exactly clear but the greater hardness of the acid Bessemer steels has been attributed to iron-oxide (P. C. Gilchrist). It has also been attributed to a variation in the initial structure of the steel the determining factors of which are said to be (1) the temperature of melting and refining, (2) the pouring temperature, and (3) the rate of cooling down to the solidus which governs the rate of formation and growth (nuclei number and linear velocity of crystallization) of the original grains.² This effect of the original structure persists even through the processes of heat treatment and may be connected with the distribution of phosphorus and other elements.

Comparing electric and open hearth steel, it may be said that open hearth steel requires about 0.05 per cent. more carbon, other ingredients being the same, to give the same properties.³ However, electric steel of the same composition is softer than Bessemer steel by about 15 points on the Brinell scale.

The specific influences of manganese, phosphorus, sulphur and silicon will be considered under the influence of impurities on steel.

Influence of the Size and Shape Upon the Properties.—There is a variation in the properties of commercial steel due to the conditions of rolling which becomes apparent when sections of

¹ *Journ. Iron and Steel Inst.*, 1907, No. 1, p. 181.

² BRES, *Rev. de Metallurgie*, 1913, Vol. 10, p. 797.

³ Private communication. Basic steel is referred to.

different dimensions are tested. Campbell¹ points out in this connection that "it seems certain that larger bars will give a lower ultimate strength, a lower elastic limit, a lower elastic ratio, a better elongation and a lower reduction of area." Comparing $\frac{3}{4}$ inch bars with $\frac{7}{8}$ inch bars he found an average superiority of the former in tensile strength of 1430 lbs. and in elastic limit of 1380 lbs., while the average elongation of the $\frac{7}{8}$ inch bars showed an increase over that of the $\frac{3}{4}$ inch bars by 0.99 per cent. and the reduction of area a decrease of 1.08 per cent. This increase in strength of the smaller (*i.e.* more worked) sections is undoubtedly due to the smaller grain size. Bessemer steel sheet bar is apparently very little affected by varying the thickness from 0.3 inch to 1 inch except that the reduction of area drops from 59 per cent. to 44 per cent. The tensile strength of open hearth sheet bar drops, at the same time, from 60,500 lbs. to 56,500 lbs. The elastic limit drops from 39,500 to 32,000 lbs. while the elongation remains fairly constant at 30 per cent. on 8 inches. The reduction of area is apparently very little affected below 0.6 inch but drops off rapidly from 60 per cent. to 49 per cent. at one inch.² The relation between carbon content and the thickness of plate, to meet Lloyds's specifications, is as follows:

Per cent. carbon	Thickness of plate
0.12 to 0.14	$\frac{3}{16}$ to $\frac{5}{16}$ inch
0.15 to 0.17	$\frac{3}{8}$ to $\frac{1}{2}$ inch
0.17 to 0.21	$\frac{1}{2}$ to 1 inch
0.21 to 0.24	1 to $1\frac{1}{2}$ inches.

The effect of size on the properties can be shown by the results of test bars taken from the outside and inside of a $5\frac{1}{2}$ inch axle and from a $1\frac{1}{2}$ inch bar, as follows:

	Tensile strength	Yield point	Elongation
$5\frac{1}{2}$ in. axle—Outside.....	48,000	32,000	23
$5\frac{1}{2}$ in. axle—Inside.....	44,000	27,500	32
$1\frac{1}{2}$ in. rod.....	49,000	38,000	23

The effect of thickness is taken into consideration in the specifications of forgings by lowering the tensile strength and raising the elongation and reduction of area for the larger sections.

¹ CAMPBELL, *The Metallurgy of Steel*, p. 322.

² WATERHOUSE, *Iron Age*, 1916, Vol. 97, No. 1, p. 896.

The presence of the eutectoid in steel, and its variation in amount with the carbon, affects the manner in which other properties vary; *i.e.*, the function is generally linear but with a change point at 0.9 per cent. carbon. On this account it seems advisable to consider the properties with reference to the amount of pearlite and the structural relationship of the pearlite with the other constituents.¹

Rolled or Forged and Subsequently Heat-Treated Steel.—By heat treatment is meant all the thermal manipulations, such as heating and quenching, undertaken for the purpose of altering the properties of, or of producing certain desirable properties in steel. The practice of heat treating steel is an inheritance from the middle ages, at which time it was utilized principally to produce steel which would take and keep a keen cutting edge. This art was in the hands of only a few people and its practice was kept as a closely guarded, family secret. The consequence of this was that up until the time the mysteries of heat treatment were subjected to scientific scrutiny, the heat treatment of steel was practiced to but a comparatively limited extent and today, were the heat treatment of steel to be suddenly confined to within the scope set by early tradition, the metallurgical art, as well as engineering practice, would suffer to an almost inconceivable extent. The general development and industrial application of heat treatment to the beneficiation of steel products is due, more than to any other factor, to the development of theoretical metallography, for once the fundamental principles became thoroughly understood, it was comparatively simple to disseminate the information thus gained and apply it to metallurgical and engineering practice. Thus we may well regard as the crowning achievement of the science of metallography, the present-day heat treatment of steel.

In the following we shall take up the heat treatment of steel from the standpoint of the metallographist, who considers the subject largely from the point of view of the microconstituents which are produced by the various treatments.

The Microconstituents of Heat-Treated Steel.—It will be remembered from the discussion of the iron-carbon constitution

¹ This point has been particularly emphasized by HOWE and SAUVEUR, for the mechanical properties of steel, and by TAMMANN (*Metallographie*) and SALDAU (*Journ. Russ. Met. Soc.*, 1916, Vol. 3, p. 112 through *Chem. Abs.*) for certain of the physical properties.

diagram that steel at high temperatures exists as a solid solution of carbon (the form not known at present) in γ iron, and, further, that this solid solution, known as austenite, splits up on cooling into ferrite and cementite. Just as it is possible, by rapid quenching, to suppress the eutectoid transformations in the copper-tin and copper-aluminum series, so also is it possible to suppress the transformation of austenite into ferrite-cementite. In the case of copper-tin alloys, suppressing the transformation is analogous to retaining the structure at room temperature which was stable at high temperatures, at least in so far as is now known, but in the case of the iron-carbon alloys, quenching does not retain the high temperature phase and we have, instead, a



× 540

FIG. 60.—Austenite etched at 1050°C. (Wark, by permission of Dr. Howe.)

series of constituents intermediate between the high temperature and low temperature phases. The assumption from this is that austenite, at temperatures below the line P-S-K, is very unstable, but that the tendency of the low temperature phases to form, given by the nuclei number and the velocity of crystal growth, is relatively small.

Austenite.—Austenite, at high temperatures, undoubtedly has a simple polygonal structure. This has been demonstrated by etching steel at 1050°C., the result of which is shown in Fig. 60.¹ So far it has proven impossible by rapid quenching to preserve this structure in ordinary iron-carbon alloys at room temperature. This can be done only in case other elements are

¹ WARK, *Metallurgie*, 1911, Vol. 8, p. 734.

added, such as manganese and nickel, both of which retard the break-down or lower the transformation temperature. Maurer,¹ by quenching a high-carbon steel containing 1.94 per cent. carbon, 2.20 per cent. manganese, 0.98 per cent. silicon from 1050°C. in ice water, was able to retain the structure of homogeneous austenite. In this condition the steel is nearly non-magnetic and soft, it being only slightly harder than a mild steel containing 0.14 per cent. carbon and 0.46 per cent. manganese.² Under ordinary circumstances when steel (that is, steel containing the normal amount of manganese) is quenched from the γ field, instead of the solid solution being retained, other constituents, about to be described, are formed. It is due to these constituents (not to the retention of austenite) that we are able to secure the remarkable properties of heat treated steel—the toughness of construction steels and the hardness of cutting tools.

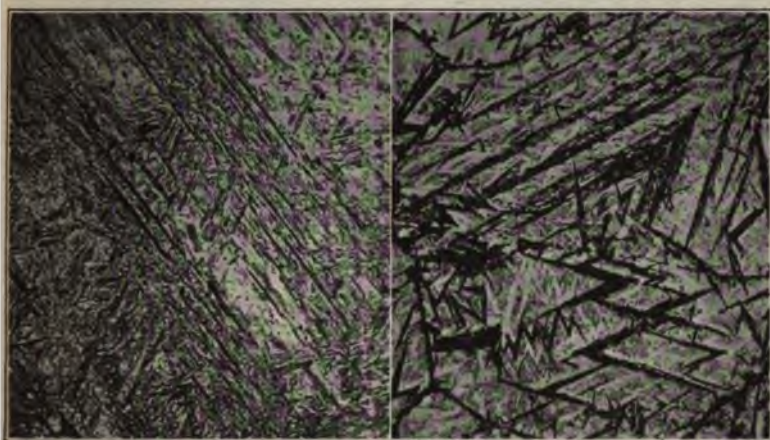
The nature or constitution of the γ solid solution, and in particular the form of the dissolved carbon, has been the subject of considerable controversy from time to time. This question will not be considered at length here, but it should at least be remarked that our present experimental means render it well nigh impossible to settle the question. Frequently the idea is advanced that inasmuch as iron carbide separates out of austenite and, further, that iron carbide and iron unite to produce austenite, the solid solution must contain carbon as the carbide. The logic of this reasoning is faulty and the procedure would not be followed, for example, in a physico-chemical study of aqueous solutions. In any event, it seems inconsistent to draw conclusions as to the homogeneous equilibrium of austenite from the phases which separate out of it. The separation of Fe_3C from the γ solid solution is simply a demonstration of the fact that austenite as a phase is able to form and grow under the existing conditions, but the conclusion does not follow that it, as a molecule, was ever present in solution. The remaining out of solution of a new phase under practically the same conditions, even when the growth is arrested, although a stable phase was not formed, does not give us a clue as to what may have been present in the solid solution prior to the change. Neither phenomenon gives any information as to the nature of the solid solution. To throw light upon this question we must turn to the iron-salt system.

¹ *Trans. Am. Inst. Min. Engrs.*, 1907, 20, 103.

² *Trans. Am. Inst. Min. Engrs.*, 1907, 20, 103, p. 23.

Brine of certain concentrations separates out salt, but we do not conclude therefrom that salt is in solution as NaCl (undissociated); in fact it is well known that such an assumption would be erroneous. A very thorough discussion of this subject is given by Guertler in his *Metallographie*, Vol. I, Pt. 2, which aptly brings out the necessity of distinguishing between phases, such as the melt, the γ solid solution, graphite flakes, crystals of Fe_3C , etc., and molecules, such as Fe_n , C_n , $(\text{Fe}_3\text{C})_n$, where "n" is supposedly some small integer. A very great amount of confusion is caused by lack of clarity on this particular point.

Before proceeding to the discussion of the micro-constituents produced in steel by heat treatment, it may be well to remark that



×270

FIG. 61.

×150

FIG. 62.

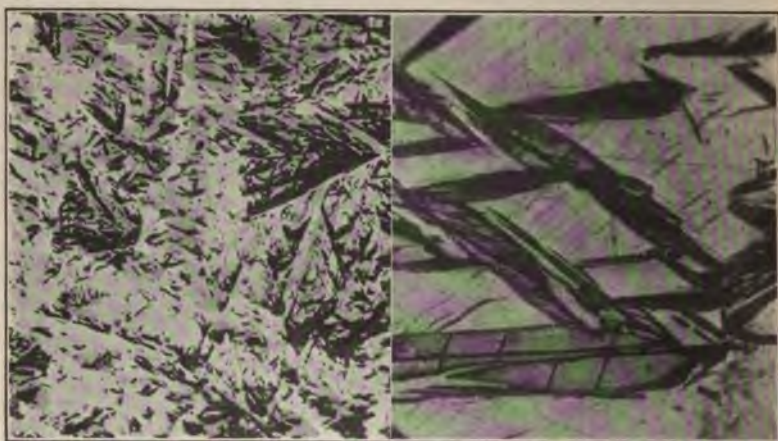
FIG. 61.—Martensite in medium carbon steel quenched from 1200°C . — (Hanemann.)

FIG. 62.—Martensite in high-carbon steel. (Hanemann.)

the tendency of one of these constituents to change into the next one is greatly affected by the chemical composition; in ordinary steels, principally by the carbon and manganese. Thus the addition of carbon and manganese acts as a brake with the apparent effect of stabilizing the metastable condition.

Martensite.—Martensite is the common constituent of steel which has been quenched in water from the γ field. Its characteristic structure in medium-carbon steel is shown in Fig. 61, and in high-carbon steel in Fig. 62. This structure is commonly

referred to as "needle-like" or acicular structure. It is said that this constituent can also be prepared from Maurer's austenite by mechanical deformation at ordinary temperatures, by reheating to about 400°C. or by plunging the metal into liquid air.¹ Of the latter there can be no doubt. Fig. 63 shows the surface of a microsection which was originally almost entirely austenite, after treatment in liquid air. The formation of martensite is accompanied by an increase in volume and the martensite needles



×150
FIG. 63.

×1040
FIG. 64.

FIG. 63.—Steel with 1.79 per cent. carbon quenched from 1160°C., polished and dipped 1 min. in liquid air. Martensite in relief on polished surface. (Hanemann.)

FIG. 64.—Austenite (light) and martensite (dark) in quenched high-carbon steel. (Hanemann.)

stand up above the original surface in strong relief. The most striking characteristics of martensite, in contrast to either austenite or slowly cooled steel, are its great hardness and excessive brittleness. Of course if the carbon content is less than about 0.45 per cent., these characteristics are less pronounced, as it is well known that a low carbon steel cannot be materially hardened by quenching.

The exact nature of martensite is a point which is still under discussion so that nothing final can be given at the present

¹ See MAURER AND LE CHATELIER, *Compt. Rend.*, 1907, Vol. 146, p. 824. The photographs published, which do not include the liquid air treatment, certainly do not indicate the formation of martensite.

writing. It is usually held to be a solid solution, and with considerable justification—see Fig. 61. The solvent is assumed to be either α iron (Le Chatelier¹) to explain the magnetism, or β iron (the allotropists²) to explain the hardness, or part α and part β iron in varying amounts to explain the increase in hardness and decrease in magnetism as the amount of carbon increases (Osmond³). That it is a separate phase from austenite is the general assumption, supported in particular by Hanemann⁴ who conducted experiments to demonstrate the difference. He pointed out the difference between austenite and martensite in magnetic properties and drew the conclusion that martensite could not contain γ iron. He further showed that of austenite and martensite, when coexisting (see Fig. 64), martensite has the lower carbon content making it perfectly clear that the two are separate phases.⁵ It has been suggested by Edwards that austenite and martensite are one and the same phase, the apparent difference being due to twinning.⁶ This reasoning is hardly as impressive as Hanemann's demonstration of precipitating the carbide from the austenite and martensite and showing that martensite contains the smaller amount. This effect is shown in Fig. 65.

Hanemann further points out that on quenching we can have the ideal conditions for the formation of metastable but rapidly forming phases; while, on slower cooling, the more sluggish but stable phases would form. The "needle-like" structure of martensite in high carbon steels is undoubtedly due to its formation in the definitely oriented austenite.

If a conclusion were to be drawn at the present time regarding the nature of martensite, the one which appears to be most rational, in the opinion of the present writer, is that martensite is a metastable, allotropic modification of the γ solid solution—

¹ *Rev. de Metallurgie*, 1908, Vol. 5, p. 167.

² See HANEMANN, *Stahl u. Eisen*, 1913, No. 2, p. 1350; *Intern. Z. Metallographie*, 1912-13, Vol. 3, p. 127.

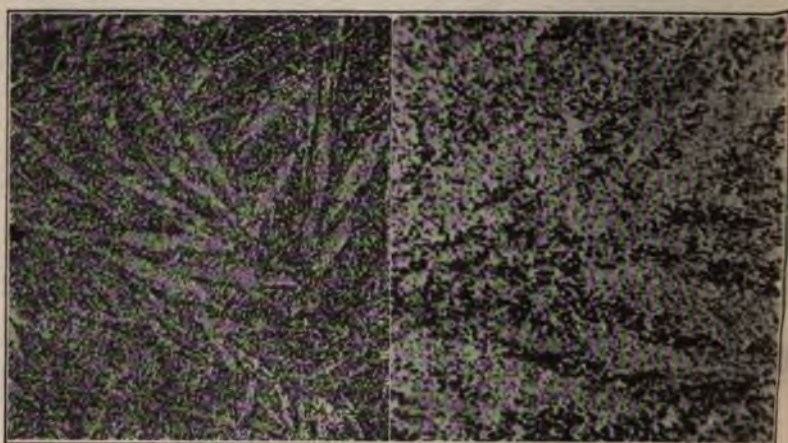
³ *Rev. de Metallurgie*, 1908, Vol. 5, p. 205.

⁴ *Loc. cit.*

⁵ See HANEMANN, *Metallographie und Wärmebehandlung*, 1915, p. 72.

⁶ *Journ. Iron and Steel Inst.*, 1910, No. 2, p. 147. This reasoning is not held to be valid by DESCH who remarks that the acicular structure accompanies but does not cause hardness—a very logical conclusion. *Trans. Faraday Soc.*, 1915, Vol. 10, p. 255.

austenite.¹ If this is so, then martensite bears the same relationship to austenite as α tridymite does to β_2 tridymite in SiO_2 .² The points which lead to this view are (1) austenite and martensite are separate phases, and (2) both may have the same composition, which occurs when a steel is first 100 per cent. austenitic and then 100 per cent. martensitic and yet (3) during the transformation, during which time austenite and martensite coexist, they are of different composition. The transformation, then, is analogous to the polymorphic transformation of a solid solution



×300
FIG. 65a.

×840
FIG. 65b.

Steel with 1.5 per cent. carbon, quenched from 1200°C. and drawn at 650°C., etched with sodium picrate. Light areas were formerly martensite needles. (Hanemann.)

and hence the present conclusion seems to be logical. As to the condition of the iron in the solid solution (martensite), it is believed that only an opinion can be expressed because we don't know now in just what particular manner α iron differs from γ iron. However we do know that there are strong forces tending to convert γ iron into α iron and so it would seem that during the

¹ According to the theory advanced by BRONIEWSKY, martensite is a stable phase, a solid solution of carbon in α iron with a very narrow range of stability (C content) at room temperature and a wide range of stability at low temperatures. It also occurs as a supersaturated solution when austenite is rapidly cooled—the usual method of preparation. See *Compt. Rend.*, 1916, Vol. 162, p. 917.

² C. N. FENNER, *Amer. Journ. Science*, 1913, Vol. 36, p. 331.

austenite = martensite change, the iron must have changed from the γ form to the α form. This opinion corresponds to that of Le Chatelier, which will be considered later.

Hardenite.—It has been shown by Hanemann that pearlite, if heated to just above Ac_1 , and quenched without too much delay, gives a structure which is quite homogeneous and structureless. If the steel is held above Ac_1 for any appreciable time, and quenched, the well-known martensitic structure forms. This he explains as being due to the coalescence of the grains of austenite into larger grains, which on quenching produce a visible martensitic structure.¹ This structureless martensite of composition 0.9 per cent. carbon he calls "hardenite," following Arnold who first proposed the name. Hardenite is the desirable constituent in quenched steels of this range of composition (cutlery steel) and the presence of a definite martensitic structure would indicate overheating.

The fact that structureless martensite—hardenite—always has the eutectoid composition is readily explained. Steel, regardless of its composition, when heated to just above the eutectoid temperature produces austenite with 0.9 per cent. carbon. If the steel is rapidly quenched before the austenite increases materially in grain size, the structure will be hardenite, either free or with excess ferrite or cementite according to the total carbon content. This hardenite will contain just 0.9 per cent. carbon. Now if the steel, either hypo- or hyper-eutectoid, were to be heated to a higher temperature to change the composition of the austenite and therefore possibly of the hardenite, the high temperature involved would increase the grain size of the austenite and quenching would no longer produce hardenite, but martensite. So hardenite, when it is formed, is always produced under such conditions that its carbon content is 0.9 per cent., the eutectoid ratio.

The original conception of hardenite was that it is a definite chemical compound, a sub-carbide $Fe_{24}C$ (Arnold). It was so called because it is the characteristic structure of properly hardened high-carbon steel. The objection to the hypothecation of a definite chemical compound, $Fe_{24}C$, for this material, is that it is

¹ HANEMANN points out in this connection that the coarseness of the martensitic structure depends largely on the size of the austenite grains, which is quite in accord with the theory of the formation of WIDMANSTÄTTIAN structure, to be discussed later.

a reversion to the original and false conception of Guthrie that eutectics are definite chemical compounds. The constancy of the composition of hardenite has already been explained.¹ The principal difference between Hanemann's conception of hardenite and Arnold's is that according to the former, hardenite forms during the quench while according to the latter, it is stable at the high temperature and is merely retained by quenching.

Troostite.—Troostite is the name given to the third constituent in the series from austenite to ferrite + cementite. Its exact nature is also in doubt. Whereas martensite should be regarded as a phase forming under certain definite conditions, troostite should be regarded as a true decomposition product of either austenite or martensite. This suggests a relatively rapid rate of decomposition of austenite and martensite but a relatively slow rate of formation of ferrite and cementite.

In general we have two methods of producing troostite in steel. Troostite forms on quenching low- and medium-carbon steels in water when the velocity of decomposition of the martensite is sufficient to produce a certain amount of disintegration, even during the brief interval of time which elapses during the quench. Benedicks states that if a test piece is wound with iron wire so as to retard the time of cooling from 725°C. to 100°C. to 9½ seconds, the steel is composed entirely of troostite. The disintegration into troostite may also be produced by heating martensite to temperatures below 400°C. The principle underlying this change is that martensite at room temperature is extremely persistent, but that as the temperature is raised, it loses its apparent stability and passes to the first stage in the change to the stable state—ferrite + cementite. It has been recently shown that this change is apparent even as low as 100°C.,² while at 200°C. the change proceeds quite rapidly.

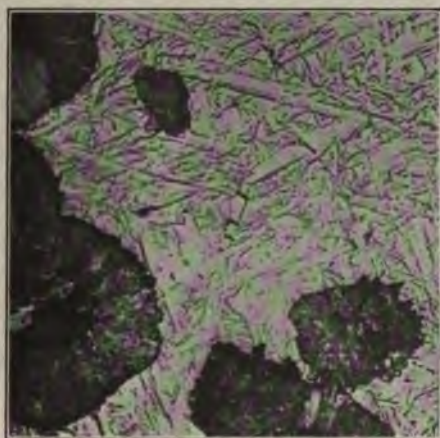
The common occurrence of troostite as a decomposition prod-

¹ It is only fair to state that Prof. ARNOLD apparently no longer adheres to the original sub-carbide theory as it is now referred to by him as a solid solution. *Trans. Inst. Mech. Eng.*, 1915, p. 290.

² SCHOTTKY noted a sudden rise in temperature of ca. 0.5°C. as a piece of quenched steel was reheated to nearly 100°C.—*Ferrum*, 1913, Vol. 15, p. 274. The same effect has been recorded by BRUSH who noted that the temperature of quenched steel which is heated to 100°C. is slightly above that of the bath, *Proc. Am. Phil. Soc.*, 1915, Vol. 54, p. 154; see also BRUSH, and HADFIELD, *Proc. Roy. Soc.*, 1917 A, Vol. 93, p. 188.

uct of martensite is shown in Fig. 66. This steel was quenched in water from above the transformation range. It is quite evident that the decomposition commences at points along the grain borders of the martensite and progresses by uniform radial growth. The result obtained by the method of quenching to produce martensite, followed by reheating to some temperature below $400^{\circ}\text{C}.$, is shown in Fig. 67. In technical practice the latter method is the one which is used when it is desired to produce troostite as it is the more reliable and gives more constant results.

The most acceptable theory relative to the nature of troostite is the one advanced by Benedicks, which is that martensite,



×450

FIG. 66.—Martensite, light, and troostite, dark. (Hanemann.)

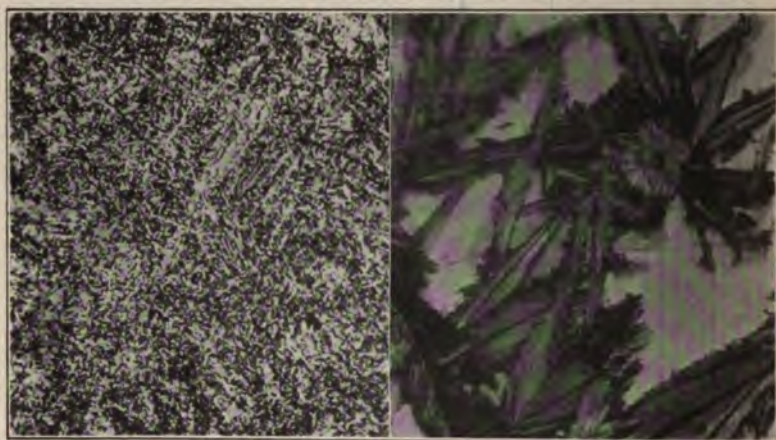
while decomposing, forms a colloidal system of cementite in a very fine state of division in α iron.¹ This solid colloid is troostite. McCance² came to the conclusion that the iron in troostite is amorphous iron which has not yet attained the crystalline state of ferrite. This amorphous iron would form from the martensite and, since carbon is insoluble in α iron, it is deposited in situ as $(\text{Fe}_3\text{C})_2$. As the transformation proceeds further, *i.e.*, as the rate of cooling becomes slower or as the reheating temperature is raised, the α iron crystallizes as ferrite and the carbide, with

¹ *Zeit. Chemie Ind. Colloid*, 1910, Vol. 3, p. 290.

² *Engineering*, 1910, Vol. 90, p. 905.

increasing polymerization, forms ordinary cementite (Fe_3C), until finally the next constituent, sorbite, is formed.

Austenite on being heated breaks down, apparently, in much the same manner as martensite. This has been followed by Hanemann who used a steel containing 1.5 per cent. carbon which had been quenched so as to produce a mixture of austenite and martensite. The austenite was found to break down sharply on reaching 270°C ., although this temperature probably would be different for other steels. The decomposition sets in at the crystal boundaries, and especially at the contact with a stable phase, such



× 500

FIG. 67.

× 80

FIG. 68.

FIG. 67.—Troostite in properly tempered steel. (Hanemann.)

FIG. 68.—Steel with 1.5 per cent. carbon quenched from 1220°C . and tempered at 260°C . Martensite has changed to troostite; austenite is commencing to decompose. (Hanemann.)

as cementite, or with troostite which has already formed from martensite. This effect is shown in Fig. 68. Martensite commences to decompose at 100°C . which temperature is sufficient to make the needles etch noticeably darker. This darkening increases with the reheating temperature until at 400°C . it reaches a maximum. Austenite decomposes in an orderly way by a gradual break-down which starts at a definite temperature and at individual points while martensite, on the other hand, seems to possess no definite decomposition temperature and the formation of troostite is general throughout the entire mass. The needle-like structure of martensite is not necessarily effaced

by conversion into troostite and may be seen in steels which have been reheated to 400°C.

Troostite is of technical importance on account of its combination of hardness with a moderate amount of toughness, so it is associated with the heat treatment of high carbon steel.

Sorbite.—By continuing the reheating of martensite to temperatures above 400°C., or by retarding the rate of cooling on quenching austenite, troostite is converted into what is undoubtedly a sub-microscopic mixture of cementite and ferrite. This aggregate is known as sorbite. Its coloration on etching is not as dark as that of troostite. The physical and chemical



X 500

FIG. 69.—Steel with 0.65 per cent. carbon, quenched from 850°C. and drawn at 600°C. Uniform sorbite. (Hanemann.)

properties of sorbite are quite different from those of troostite so that, while its appearance is very similar under the microscope, there is little doubt that it is a different constituent.

The structure produced by heating martensite to temperatures above 400°C. is shown in Fig. 69. The structure produced by quenching austenite in oil is shown in Fig. 70. It will be noted here that a rate of cooling which is slow enough to produce sorbite (in medium-carbon steel) is so slow that a certain amount of free ferrite separates out as a net-work. The normal structure of this steel is shown in Fig. 56-b. The true difference in structure of the dark constituent is brought out only under the high magnification.



FIG. 70a.

FIG. 70b.

Steel with 0.40 per cent. carbon quenched in oil from 850°C. Ferrite net-work plus sorbite.



×800

FIG. 71.—Steel with 0.40 per cent. carbon heated to 900°C., cooled in furnace to 715°C., quenched in water. Etched three hours in hot sodium picrate. Ferrite light and martensite dark.

It has been asserted by the Nomenclature Committee of the International Association for Testing Materials that sorbite is produced by rapid quenching from just above the lower critical point. To the writer's mind this statement runs counter to the laws of heterogeneous equilibrium, as applied to this system, and should be accompanied by positive evidence of the fact. Furthermore the structure obtained by the writer by this treatment is ferrite plus martensite; the ferrite from the primary ferrite stable above A_{r_2} and the martensite from the austenite containing about 0.9 per cent. carbon. This structure is shown in Fig. 71.



FIG. 72.—Granular pearlite. Cementite occurs as spheroids. (Hanemann.)

After considerable experimenting it was found that the structure could be developed by a prolonged treatment in hot sodium picrate.

Sorbite is of technical importance on account of its remarkable combination of strength, ductility and toughness, particularly notch toughness. Consequently sorbite is associated with the heat treatment of medium-carbon steel, or forging and machinery steels.

Granular Pearlite.—By reheating quenched steels up to temperatures just below 700°C . the particles of cementite grow by coalescence until they become visible under the microscope. This structure, shown in Fig. 72, is known as granular pearlite. The phases are the same as those in sorbite and ordinary lamellar pearlite. This condition corresponds to the softest, weakest,

and most ductile state which the steel can assume at normal temperatures. Granular pearlite is considered to be structurally stable so that it represents the condition which all steels tend to assume at temperatures below the transformation point. It has been pointed out by Hanemann and Morawe,¹ reviewing previous work, that granular pearlite can form in three other ways besides the one just described—(1) by very slow cooling past A_{r1} ; (2) by repeatedly heating and cooling through A_{c1} and A_{r1} ; (3) by long annealing of lamellar pearlite at temperatures

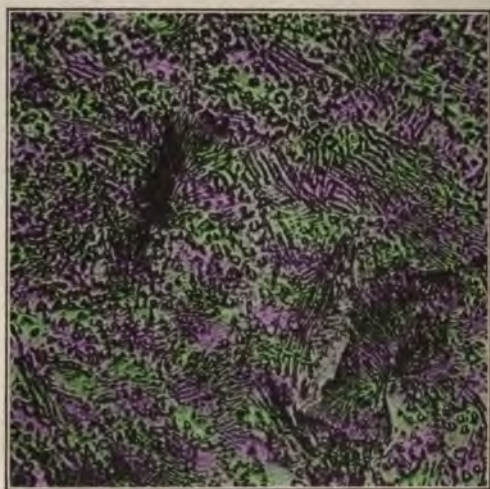


FIG. 73.—Lamellar pearlite changing to granular pearlite. Divorce annealing. (E. Leitz.)

just beneath A_{c1} . The latter case, in an early stage, is shown in Fig. 73. It is referred to by Howe as "divorcing" annealing.² This spheroidizing has a marked softening effect on pearlite as is brought out by the work of Ishewsky³ who showed that the tensile strength drops from 109,000 pounds to 76,500 pounds per sq. in. and that the elongation increases from 11.8 per cent. to 19.75 per cent. The carbon content was 0.83 per cent.

¹ *Stahl u. Eisen*, 1913, Vol. 33, p. 1350. Lack of structural stability of lamellar pearlite was discussed by OSMOND, *Rev. de Met.*, 1904, p. 349. The stability of granular pearlite was thereupon demonstrated by GOERENS, *Met.*, 1907, Vol. 4, p. 182, who annealed lamellar pearlite just below the transformation range and converted it into granular pearlite. This point has also been discussed by BENEDICKS.

² *Proc. Cleveland Inst. Eng.*, 1913-14, p. 218—a comprehensive treatise.

³ *Intern. Journ. Met.*, 1914, Vol. 6, p. 199.

It has been stated that the transitions just described, from austenite through martensite to pearlite, also take place on slow cooling,¹ which seems to make it necessary to believe that lamellar pearlite forms from sorbite. On theoretical grounds, from the rate of decomposition of the products, it would be difficult to explain the formation of martensite and troostite at the high temperatures of the transformation range. Moreover sorbite is phasially stable and when it changes, as we well know, the change is purely structural and the resulting product is granular pearlite. Sauveur states² that the transformations in steel on slow cooling take place in the following order: at Ar_3 the iron changes from its γ form to its β form, by which is meant that austenite changes to martensite, and between Ar_3 and Ar_2 , the β solid solution (martensite) separates out β iron. The idea here is that it must be a solution of β iron and not of γ iron which separates out β iron. At Ar_2 there is some β iron and some martensite. During the Ar_2 change the β iron changes into α iron and the martensite changes into an α iron solution, said to be troostite. Between Ar_2 and Ar_1 , α iron separates from troostite until at Ar_1 there is some α iron and troostite. At Ar_1 the troostite changes into pearlite. In this conception of the transformations it is not conceded that the γ solid solution, in the case of a low carbon steel, continues to exist below Ar_3 , and that by increasing in carbon it finally reaches 0.9 per cent. carbon at Ar_1 , and that it is this austenite, with eutectoid composition, which transforms into pearlite. The principal reason for rejecting the usual theory is said to be that the Ar_3 critical point represents, not the beginning of a reaction, but a complete reaction in itself.

Steel of eutectoid composition is supposed to form first martensite, then troostite and then pearlite, by change in the iron from γ to β to α and then finally the splitting up into α iron and Fe_3C .

This conception disregards, completely, the laws of heterogeneous equilibria and the phase rule. First of all, even on slow cooling, we may not justifiably assume conditions of perfectly stable equilibrium but we may assume that the phases and the phasial successions are stable, *i.e.*, that they are not metastable.

¹ See TAMMANN, *Lehrbuch der Metallographie*, 1914, p. 258. Also SAUVEUR, *Metallography*, 1916.

² *Journ. Iron and Steel Inst.*, 1906, No. 2; also *Metallography*, Second Edition, p. 196.

Therefore if a solution of β iron forms, which may or may not be martensite, it must be a stable phase. Now this β iron solution is supposed to separate out β iron, another stable phase, and we must therefore assume a monovariant equilibrium between β iron and the β iron solution. Such an equilibrium is impossible, as no simple substance (phase) can be in equilibrium with the (saturated) solution of another element in that substance. Water cannot be in equilibrium with brine (liquid water + salt) and the coexistence of two such phases would imply incomplete equilibrium which, by diffusion, would soon produce a less concentrated solution of salt in water. So it is not only unnecessary, but also contrary to fact, to assume that the γ solid solution

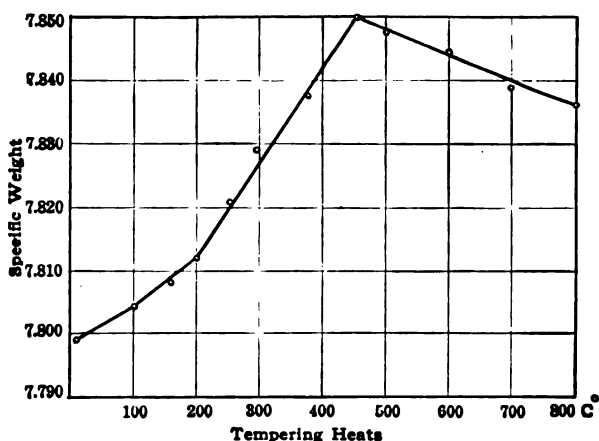


FIG. 74.—Steel with 0.83 per cent. carbon quenched at 800°C. Change in specific gravity with drawing temperature. (Maurer.)

changes to a β solid solution and it is accepted here that austenite separates out β or non-magnetic iron, and concentrates in carbon. It might be argued here that the analogy is not strictly accurate, that it is not water, but ice, which separates out of the brine. The reply would be that neither is the brine solution one of salt in ice but one of salt in water. In other words, the substance segregating is in a different state from that of the solute, which is all that is being argued here.

Secondly, a four-phase equilibrium is assumed at Ar_2 which is an impossible case in a two-component system. It is held that further discussion of this conception is unnecessary but we may use it as illustrating the necessity of using the phase rule and the

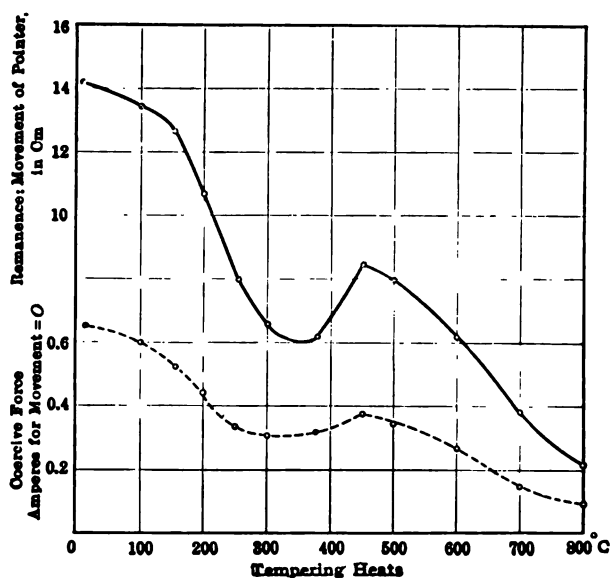


FIG. 75.—Steel with 0.83 per cent. carbon, quenched at 800°C. Change in remanence and coercive force with drawing temperature. (Maurer.)

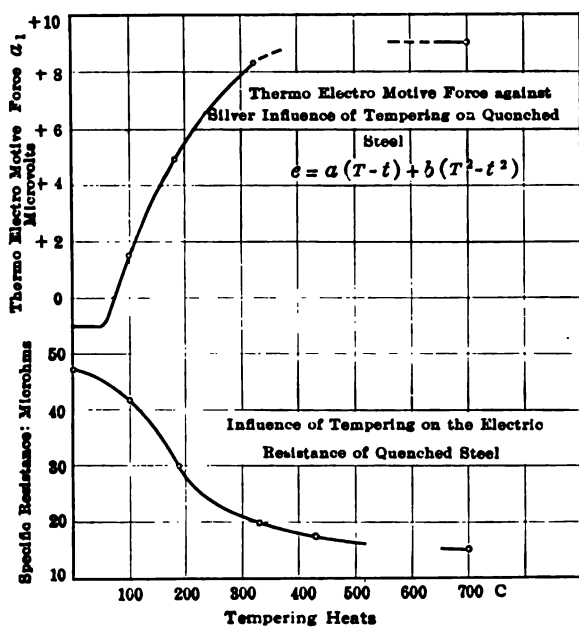


FIG. 76.—Effect of drawing temperature on the electrical properties of quenched steel. Curves by Barus and Strouhal. (Heyn and Bauer.)

laws of heterogeneous equilibria as our fundamental guide in treating transformations and of treating variations or exceptions as due to the intercession of other laws of nature involving the kinetics of transformations.

The effect of reheating on the properties of quenched steel has been a fruitful field of research and the results of this work have thrown considerable light on the phenomena in question. A summary of this work, taken from Heyn and Bauer, is reproduced here. The effect of tempering temperature on the specific gravity, magnetic properties, the specific resistance, the thermal electromotive force, the hardness, the rate of dissolution in sulphuric

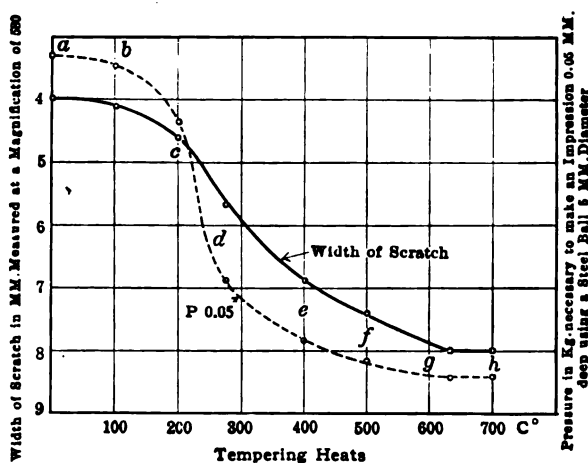


FIG. 77.—Steel with 0.95 per cent. carbon, quenched at 900°C. Effect of drawing temperature on the ball and scratch hardness. (Heyn and Bauer.)

acid and the condition of the carbon are given in Figs. 74 to 79. These curves bring out the difference in tempering temperatures between troostite and sorbite. The constituent formed at 400°C., which gives the darkest coloration on etching, has been called osmondite by Heyn and Bauer. Those interested in a more complete account of this work should refer to the *Journal of the Iron and Steel Institute* for 1919, No. 1.

The following table is added to give an idea of the relative mechanical properties of the various microconstituents of the iron-carbon alloys. The range in hardness of martensite is at once apparent. Inasmuch as hardness is so closely related to the constitution of steel, we shall consider it at this place.

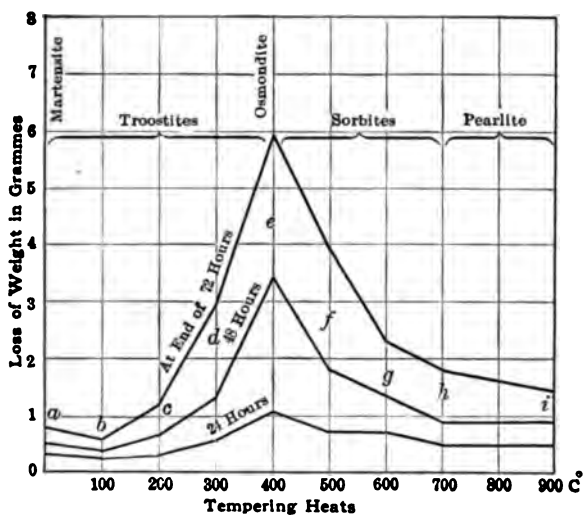


FIG. 78.—Steel with 0.95 per cent. carbon, quenched at 900°C. Effect of drawing temperature on the rate of solution in 1 per cent. sulphuric acid. (Hegn and Bauer.)

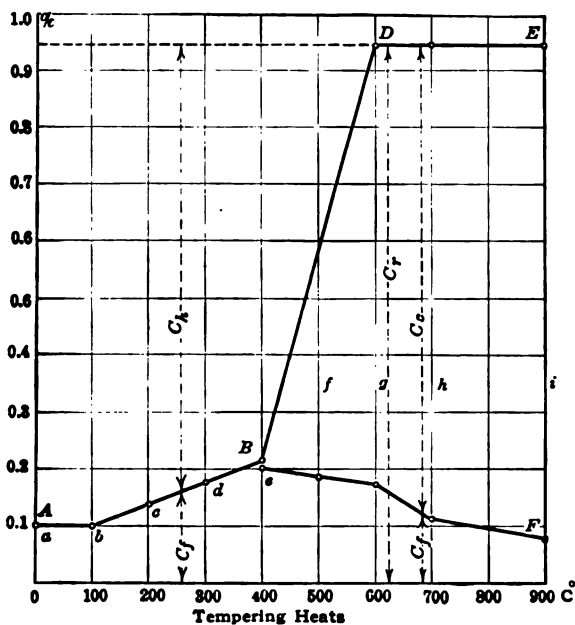


FIG. 79.—Steel with 0.95 per cent. carbon, quenched from 900°C. Effect of drawing temperature on behavior of carbon on dissolving in 10 per cent. sulphuric acid out of contact with air.

C_A = carbon evolved as hydrocarbons = total carbon - C_r

C_r = carbon remaining in residue.

C_f = carbon in residue after treating C_r in hot HCl.

$C_c = C_r - C_f$ = carbide carbon.

TABLE 38.—HARDNESS OF THE MICROCONSTITUENTS OF STEEL BOYNTON

Constituent	Tested in	Hardness number
Ferrite.....	Electrolytic iron	1
	Electrolytic iron, quenched	2.15
	Wrought iron	1.5- 3.6
Pearlite.....	Steel with 0.13-1.52 per cent. C.	1.8- 10.3
	Steel with 0.35-0.86 per cent. C.	3.8- 4.2
Sorbite.....	Steel with 0.48-0.58 per cent. C.	5.2- 53.6
Troostite.....	Steel with 0.58 per cent. C.	88.2
Martensite.....	Steel with 0.20-1.52 per cent. C.	38.9-261.6
Austenite.....	White cast iron with 3.24 per cent. C.	103.4
Cementite.....	Grey cast iron with 3.24 per cent. C.	272.8

In this table electrolytic iron is assumed to be unity. The relative hardness was determined with the Jaggard micro-sclerometer.

The Hardness of Quenched Steel.—Many theories have been advanced to explain the excessive hardness of quenched high-carbon steel. Among these may be mentioned the carbon theory, the allotropic theory, the mechanical strain theory, the solid solution theory, and the sub-carbide theory.

The Carbon Theory.—Two of the earliest theories advanced were the carbon theory and the allotropic theory, both of which were strongly supported by their respective adherents. These two camps were called, respectively, the "Carbonists" and the "Allotropists."

The "Carbonist" assumed that there exist two forms of carbon-carbide carbon of annealed steel and hardening carbon of quenched steel. Hardness was said to be due to the hardening carbon present, retained by quenching the steel in water from a red heat. On slow cooling the hardening carbon would change to carbide carbon and the steel would be soft. The difference in the form of the carbon could be noted by treating the steel with cold dilute acid which would drive off the hardening carbon as a gaseous hydrocarbon but would leave the carbide carbon as a residue analyzing Fe_3C . This theory is now no longer tenable in the light of the fact that quenched steel loses 70 per cent. of its hardness on reheating before any carbon changes to carbide carbon.¹ Furthermore a quench so rapid that the form of the carbon would remain unchanged would not produce hardness, even in high carbon steels.

¹ See HEYNS, *Journ. Iron and Steel Inst.*, 1909, No. 1, p. 109.

The Allotropic Theory.—The “Allotropists,” headed by Osmond, assumed the existence of a hard allotropic form of iron, said to be β iron, and further that β iron could be retained on quenching if enough carbon were present. Hardness would be due, then, principally to the retention of the β iron, and the function of carbon would be to retard the break-down of the solid solution.

A modified form of the allotropic or β iron theory, which has numerous adherents, has more recently been stated by its author, Osmond.¹ The principal factors in the hardening of steel are held to be (1) the retention of carbon in the metastable condition of hardening carbon; (2) the partial retention of an allotropic modification of iron which is also metastable at ordinary temperatures; (3) mechanical strains formed in consequence of the change in volume which accompanies the partial transformations. Osmond assumes that the effect of carbon on the properties of hardened steel is practically nil. Since the hardness produced by quenching has lost more than 70 per cent. of its intensity after tempering below 400°C., hardening would be due to a certain amount of strain hardened α iron and allotropic β iron, the former accounting for part of the hardness and the magnetism and the latter for the majority of the hardness of quenched steel. As the carbon content increases, the ratio of β to α iron increases, explaining the increase in hardness and the decrease in magnetism. The recalescence of quenched steel on reheating would be explained as due to the change from β to α iron.

The Solid Solution or α Iron Theory.—Le Chatelier assumes that carbon is retained in solution on quenching but that the iron is in its α form, with which he explains the magnetism of martensite. Hardness is supposed to be due to the solid solution. The hypothecation of a hard β iron is not used in this theory. The recalescence on reheating quenched steels in this case would be due to the break-down of the solid solution.

The Sub-Carbide Theory.—The theory has been advanced by Arnold that iron and iron carbide form a sub-carbide Fe_{24}C which is retained by sudden quenching and confers its property of hardness on the steels. This theory was interesting in its time but is no longer of service since the laws of heterogeneous equilib-

¹ *Rev. de Met.* (Mem.), 1906, Vol. 3, p. 447.

rium have been applied to the investigation of the constitution of metallic alloys.

The Mechanical Strain Theories.—These theories account for the hardness of quenched steel as being due to contraction strains on cooling and to the formation of the bulkier martensite. The effect of pressure on the hardness of steels has already been mentioned but it was assumed there to produce only a minor portion of the hardness. In the theories advanced simultaneously by McCance and by Carpenter and Edwards, the stresses set up on quenching are assumed to play the leading role. These theories have been recently stated by Professor Carpenter, from whom the following is quoted:¹ "In quenching such alloys as iron-carbon steels, severe stresses are set up which cause very pronounced crystal twinning. This twinning appears to be directly connected with the intensity of the thermal changes that occur when such steels are slowly cooled. The increased hardness which is produced is directly related to the velocity and thermal magnitude of the suppressed inversion and the connection between these factors, crystal twinning and carbon percentage, is very evident. At all the surfaces of slip upon which twinning occurs, amorphous layers are formed and under the conditions of hardening persist. It is considered that the ultimate cause of hardness by quenching steel is the presence of these amorphous layers. If such is the case it would follow that the final cause of hardening by quenching is exactly the same as that of hardening by cold working, viz., the internal deformation of the crystals. The hardness of any one steel would depend upon the amount of twinning that occurs but in different steels it would depend as well upon the molecular constitution of the amorphous layers."

The second theory, due to McCance, is termed the "Inter-strain Theory of Hardness." According to this theory, during the quenching of steel two transformations can take place—(a) the transformation of γ to α iron, and (b) the transformation of carbon in solution to the state of carbon out of solution. The first of these can take place independently of the second but the carbon cannot change its condition without necessitating the transformation to α iron of the γ iron in which it is dissolved. In a quenched and uniformly hardened steel the carbon is in the state of solution and it retains a portion of the γ iron in solu-

¹ HARBORD and HALL, "The Metallurgy of Steel," Vol. 1, p. 362, 5th Edition, 1916.

tion, the proportion increasing very rapidly with the carbon content. The majority of the iron is in the α condition but owing to the restricted mobility during the period of quenching, the crystalline units are not homogeneously oriented and the hardness of quenched steels is due to this condition which is similar to that of interstrain.

The principal objection to the strain theory would be that quenching from high temperatures does not necessarily produce the hardest steels. In fact, a high carbon steel quenched from just below the solidus, which certainly is in a condition of extreme internal strain, is not necessarily harder than the same steel quenched from just above the critical range. In fact, it may retain a large amount of austenite and become relatively soft. Possibly this objection is not entirely adequate because it may be assumed that the interstrain is due to a constitutional or phasial change (austenite = martensite) and not to a temperature change.

The hardness of quenched steel, according to these theories, is due to three different things—the allotropic transformations of pure iron, the change in the carbon condition, and internal strains set up during quenching. In the written discussion of these theories it is frequently difficult to tell whether phases or molecules are meant by such expressions as α iron, β iron, hardening carbon, etc. As a matter of fact, the hardening of steel by quenching is due to the formation of the phase martensite, and in order to produce any considerable hardness, this martensite must be fairly high in carbon. Now we have no means at present for determining the constitution of austenite, nor the molecular weight of carbon in solution, so, *a fortiori*, we cannot now determine the constitution of martensite and hence we cannot now say what the cause of hardening is. Suffice it to say here that it is apparently a phasial phenomenon associated with the solid solution martensite and that the hardness of martensite increases remarkably with the carbon content. As Sauveur pointed out recently,¹ “it would seem as if the methods used to date for the elucidation of this complex problem have yielded all they are capable of yielding and that further explanation of these will only serve to confuse the issue. . . . the conclusion

¹ Metallography and the Hardening of Steel, Intern. Congress Engineer, San Francisco, 1915.

seems warranted that new avenues of approach must be found if we are ever to obtain a correct answer to this apparent enigma."

Before passing, brief mention will be made of some recent work of Portevin and Garvin on an experimental determination of the transformations which occur in steel during quenching.¹ Historically this work followed similar work on alloy steels in which the transformations take place much more slowly and may be more readily analyzed. Experimentally the work consisted in determining the cooling curve of a steel quenched, in the usual manner, in water. Different rates of quenching were secured by using samples of varying diameters but geometrically similar. The result of the quench, whether troostite or martensite, was told from microscopic examination and hardness tests. In this way Portevin and Garvin showed that troostite forms at 650 deg. Cent. while the temperature remains momentarily constant. As the speed of quenching is increased, the troostite formation at 650 deg. Cent. disappears and another transformation takes place beginning at 300 deg. Cent. and continuing with fall in temperature. This transformation corresponds to the formation of martensite. The change in quenching velocity required to produce this change was found to be small; in other words the change from troostite to martensite on increasing the quenching velocity is sudden. (The difference between the transformations at 650 and 300 deg. Cent. is the same as the difference between the break-down of a solid solution into two phases and the change of one solid solution into another solid solution.)

The quenching velocity corresponding to the appearance of the low temperature transformation was termed the "critical velocity." For a steel containing 1.07 per cent. carbon and 0.08 per cent. manganese quenched from 750 deg. Cent. this critical cooling velocity was secured with a sample 13 mm. in diameter corresponding to cooling from 700 to 200°C. in 6.6 seconds ($=\tau$). Quenching a sample 14 mm. in diameter resulted in troostite at the center and a heat effect was noted at 650°C. ($\tau=6.9$ sec.). With a steel containing 0.50 per cent. carbon and 0.13 per cent. manganese quenched from 750°C. the critical cooling velocity (τ) was found to be 3.8 seconds corresponding to a diameter of 10 mm. With a steel containing 0.81 per cent. carbon and 0.21 per cent. manganese quenched from 750°C., the critical cooling velocity was found to be much lower inasmuch

¹ PORTEVIN and GARVIN, *Journ. Iron and Steel Inst.*, 1919, No. 1, p. 469.

as specimens up to 20 mm. in diameter were all martensitic. The time of quenching (τ) was 10 seconds. In general it was found that there is a minimum in the critical velocity at the eutectoid composition, assuming steels with about 0.20 per cent. manganese. In other words, the steels of eutectoid composition require less drastic quenching and are more readily retained in the hardened condition than are the hypo- or hypereutectoid steels. The retarding effect of manganese was also verified.

Concerning the effect of quenching temperature on the transformations during quenching, the following may be said. If the quenching velocity is considerably below the critical velocity, raising the quenching temperature does not eliminate the upper heat effect. Thus steel with 0.3 per cent. carbon and 0.2 per cent. manganese, 16 mm. in diameter, was quenched from 750 and 870°C. and a steel with 1.45 per cent. carbon and 0.2 per cent. manganese, 16 mm. in diameter, was quenched from 775 and 900°C., but in all cases the quench produced troostite. On the other hand, if the rate of cooling approaches the critical velocity, increasing the quenching temperature by 50 to 100°C. eliminates the troostite and produces uniform martensite. This verifies the usual assumption that raising the quenching temperature increases the rate at which the transformation range is passed through, but, as Portevin and Garvin point out, the total quenching time, τ , is increased due to the retardation at the martensite transformation at the low temperature. An important point which may be deduced from these considerations is as follows. At a certain depth below the surface of a piece of steel we will have a cooling velocity corresponding to the critical cooling velocity, consequently we may increase the depth of hardening (martensitization) by raising the quenching temperature.

It was concluded that troostite is composed of the same phases as pearlite in a very finely divided state and that troostite comes directly from austenite and not through martensite as is sometimes assumed. Referring to Fig. 66 it follows that the austenite broke down in part along the crystal borders into troostite and that the remainder transformed into martensite at a lower temperature. This seems very effectually to dispose of the assumption of complex changes on slow cooling like austenite \rightarrow martensite \rightarrow troostite \rightarrow sorbite \rightarrow lamellar pearlite, a conception the origin of which is difficult to understand.

Carbides in Steel.—That carbon occurs in annealed steel as iron carbide was described by Abel in 1885.¹ The formula Fe_3C was ascribed to it as the simplest expression of the relative amounts of iron and carbon which it contained. Whether or not this represents the molecule is not definitely known, chiefly on account of the lack of experimental means for determining molecular weight in the solid state. The carbide can be recovered from annealed steel by treatment with cold dilute mineral acids which leave behind a residue analyzing 6.66 per cent. carbon. It has long been known that if quenched steels are treated in the same way the carbon is given off as volatile hydrocarbons. This difference has long been used to illustrate the difference between carbide carbon and hardening carbon.

It has been shown by Professor E. D. Campbell of the University of Michigan, in a series of papers,² that a study of the hydrocarbons thus evolved from steels treated with dilute acid leads to a very serviceable theory of the constitution of steels and, in particular, to a theory of hardening. He has shown (A) "that in annealed steel the mean molecular weight of the hydrocarbons evolved, hence presumably of the carbides from which the hydrocarbons are derived, decrease as the percentage of carbon increases," and (B) that with a definite steel the "mean molecular weight of the hydrocarbons evolved from hardened steel is lower than that of the hydrocarbons from the same steel annealed, i.e., that the molecular weight of the carbides decreases when the metal is hardened." He has shown in another paper (C) "by a study of the di-nitro derivatives derived from the carbides in steel, that the carbides of lower molecular weight are more readily soluble in iron than those of higher molecular weight and have a greater hardening effect, but that they tend to dissociate with rise in temperature." He suggests that the dissociation is analogous to ionic dissociation in liquid solutions and the term "ionoid" is advanced to represent such dissociation. He has also shown on the same grounds that, with rise in temperature, carbides of high molecular weight "tend to split up into compounds of lower molecular weight and undergo more or less ionic dissociation." In his theory, to account for the products of

¹ *Proc. Inst. Mech. Engin.*, 1885, p. 30.

² *Journ. Iron and Steel Institute*, (A) 1899, No. 2, p. 223; (B) 1908, No. 3, p. 318; (C) 1913, No. 2, p. 367; (D) 1914, No. 2, p. 1; (E) 1915, No. 2, p. 164; (F) 1916, No. 2, p. 268; (G) 1917, No. 2, p. 251. *Journ. Amer. Chem. Soc.*, 1912, Vol. 34, p. 1159.

solution, iron is regarded simply as a metallic substitution product of the hydrocarbons, whose molecular weights and molecular constitutions will depend upon the carbon concentration and heat treatment. More recently (*D*) he points out that if the increase in specific volume of hardened steel, compared with that of annealed steel be largely due to the osmotic pressure of the dissolved carbides, then it would seem if a simple carbide Fe_3C alone were present that the increase in specific volume should be directly proportional to the increase in percentage of carbon. That the increase in specific volume is more rapid than the increase in carbon has been shown by McCance.¹ This may be accounted for "if the molecular weight of the carbide is recognized, for as the percentage of carbon increases, the molecular weight of the carbide decreases, hence the number of carbide molecules per unit volume and consequently the osmotic pressure at a given temperature would increase more rapidly than the percentage of carbon." In (*D*) the author suggests that austenite is a solid solution in which the carbides have nearly completely dissociated, and explains in this way the small effect of carbon on the physical properties. The form of the iron, the solvent, is not considered.

In paper (*E*) it was shown that the specific resistance and color carbon (amount of dinitro derivatives) decrease in a parallel manner as quenched steel is reheated.² The theory of "ionoid" dissociation was further developed and the hypothesis advanced that the decrease in electrical resistance is due to the decrease in the ionic concentration of the carbides in solution. This idea was carried out still further in a paper in the subsequent year (*F*) and it was shown that the curves for thermo-electromotive force parallel those for specific resistance. In the discussion it was shown that the release of internal strains or the recrystallization of possible amorphous material could have but a minor effect in causing the lowering of the specific resistance. The proof of this was that very severely cold-deformed ingot iron, though hard to the Brinell test (hardness number 240-250), had a specific resistance of 10.63 microhms as compared to 10.50 microhms for the annealed material. This paper also brought out that carbon in eutectoid and hyper-eutectoid steels, for equal atomic percentages, has about twice the effect that carbon in hypo-eutectoid steel has. In the latest paper of the series (*G*)

¹ *Journ. Iron and Steel Inst.*, 1914, Vol. 89, No. 1, p. 192.

² See also, *Journ. Amer. Chemical Soc.*, 1915, Vol. 37, p. 2039.

the determinations are extended to steels containing, besides carbon, silicon, nickel, and chromium.

To date, Professor Campbell's treatment of this highly complex question appears to be the most rational and promising and it is sincerely to be hoped that further work in this direction will be attempted. It would be well, in this connection, to correlate with these results, the microstructure and mechanical properties, and to consider more fully the effect of the allotropic changes of the iron on the properties of heat treated steel.¹

The Critical Points of Steel.—The temperatures at which the transformations in iron and steel occur are commonly called the "critical points." In addition to the nomenclature already given for pure iron the eutectoid inversion is called the A_1 point, Ac_1 on heating and Ar_1 on cooling. The temperature at which iron just completes dissolution in austenite on heating is Ac_2 and the temperature at which iron commences to separate out on cooling is called Ar_2 . Sometimes the cementite line is called A_{cm} and the graphite line A_{gr} .

The A_3 Line.—In medium carbon or construction steels, the A_3 point is the one of greatest technical importance, the reason being that the temperature selected for annealing or quenching is but slightly in excess of Ac_3 . However, it is difficult to determine a point of this character with any great accuracy and no entirely satisfactory method has been developed, although thermal analysis is commonly used. A series of heating and cooling curves of the carbon steels is shown in Fig. 80. The writer has made an attempt, in Fig. 81, to give an A_c diagram and an A_r diagram, to show about what might be expected for the ordinary steel of commerce. These diagrams are based largely on differential curves made with a large Weston Universal potentiometer and on the microstructure of steels quenched from various temperatures, while heating and cooling. The laboratory work was done in the author's laboratory (University of Minnesota) by Mr. Dowdell and may be said to represent standard laboratory practice. These diagrams are advanced with considerable diffidence, on the author's part, for it is so well recognized that results of thermal and micrographic analysis

¹ These questions are receiving considerable attention at the present time and it may well be, particularly with the development of radiographic analysis, that definite answers will soon be forthcoming.

depend so much on chemical composition, the conditions of the "run" and on individual interpretation of the data.

The points on heating are much more constant than those on cooling, which is fortunate, as the heating curves are the ones which would naturally be employed for the control of heat treatment. The upper critical point on cooling is of chief importance in connection with forging practice (finishing temperatures).

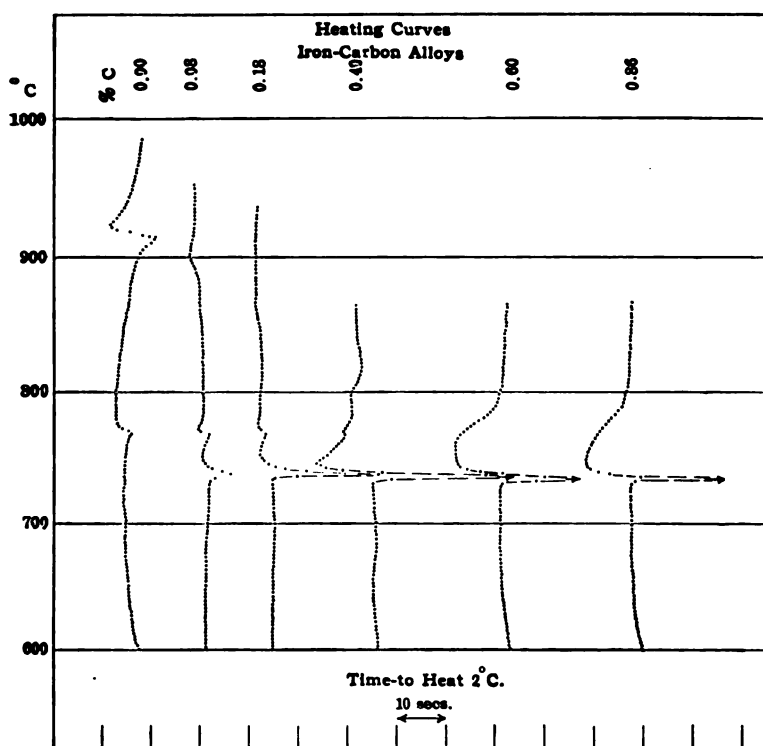


FIG. 80a.—Heating curves of steel—Bureau of Standards. (Curves by Burgess, Crowe and Scott.)

The micrographic method of locating the A_2 points is of great importance, although it is one which could not be as readily employed in control work as that of thermal analysis.

The A_2 Line.—The A_2 line is drawn at $767^\circ\text{C}.$, the temperature given by Burgess and Crowe for pure iron. Commercial steels contain some manganese and other elements so there may be occasion, at some future date, to revise the A_2 line. This

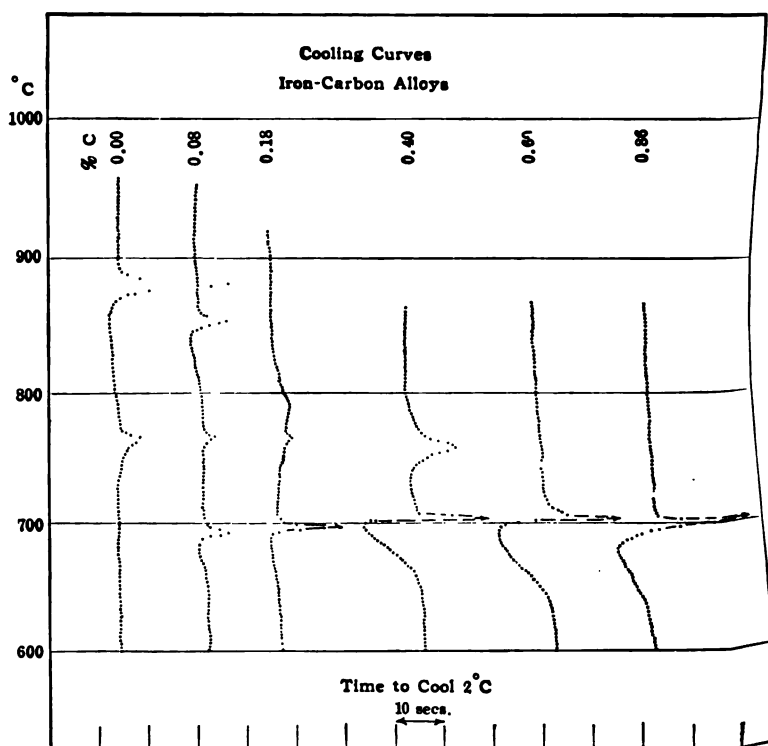


FIG. 80b.—Cooling curves of steel. Bureau of Standards. (Curves by Burgess, Crowe and Scott.)

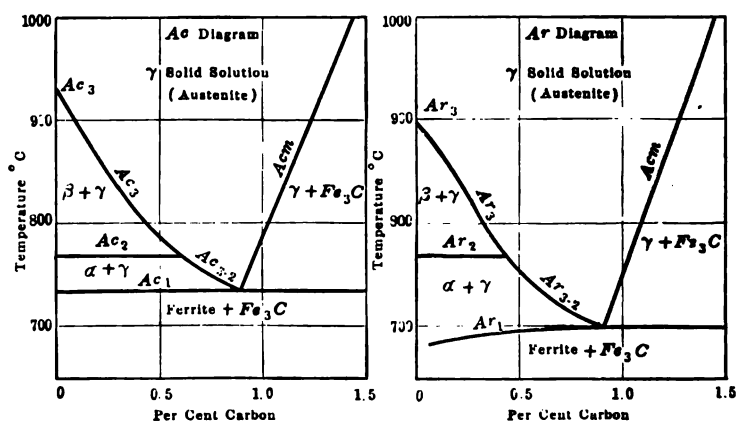


FIG. 81.—Critical point diagrams of steel.

line plays no important part in the heat treatment of steel so an approximation will be held to be sufficient for the present purpose.

The A_1 Line.—The heating and cooling curves in Fig. 80 indicate that Ac_1 comes at 735°C. and Ar_1 at 690° to 700°C. , although here again, the rate of temperature variation, amount of impurities present, and even the maximum heating temperature, affect the actual transformation temperatures. As an example of the effect of the rate of heating and cooling we may take the work of Honda¹ who found Ar_1 at 688°C. for a "normal" rate of cooling and at 721°C. for an extremely slow rate of cooling. In the same way Ac_1 was found at 730°C. for extremely slow heating. A thermo-magnetic method was used to make the determinations. This is confirmed by some recent work in the writer's laboratory by Mr. Foley. Smith and Guild who also used a thermomagnetic method, found Ac_1 at $735^\circ\text{C.} + 1^\circ\text{C.}$ for the range in carbon content from 0.1 per cent. to 1.5 per cent. The temperature cited is that of the beginning of the transformation. Ar_1 was found to decrease continuously with the carbon content from about 725°C. to about 695°C. ²

An ingenious method for determining Ac_1 and Ar_1 has been worked out by Stead.³ A steel bar, presumably with about 0.9 per cent. carbon, is heated on one end above the critical points in a porcelain tube. The temperatures at four points along the bar are determined by the points at which silver, sodium chloride, aluminum, and zinc fuse. The bar is then removed and quenched, ground smooth on one side and etched in a 20 per cent. solution of nitric acid in water. The hardened portion becomes black while the soft part becomes gray. The temperature of the dividing line (equals Ac_1) can be easily computed from the temperature observations. Ar_1 can be determined by quenching after slow cooling for a few degrees. The results obtained by this method on a steel containing 0.9 per cent. carbon and practically nothing else were $Ac_1 = 728$ to 731° , $Ar_1 = 710$ to 712° .

The A_{cm} Line.—The temperature at which cementite begins to separate out on cooling or at which it is just completely

¹ *Sci. Rep. Tohoku Imp. Univ.*, 1916, Vol. 5, p. 284.

² Paper read before the Royal Society, Feb. 12, 1914. BARDENHAUER found that Ar_1 rises from 706°C. in low carbon steel to 722°C. at 0.9 per cent. C.—*Ferrum*, 1917, Vol. 14, pp. 129, 145.

³ *Journ. Iron and Steel Inst.*, 1913, No. 2, p. 399.

dissolved on heating cannot be accurately determined by thermal analysis. The methods which have been employed are (1) annealing followed by quenching and microscopic examination to determine the structure,¹ and (2) annealing and etching with chlorine at the temperature in question, followed by microscopic examination.² These results agree fairly well with the A_{cm} line in Fig. 81 and it is drawn in accordingly.

The Effect of Manganese.—The effect of manganese is two fold, to lower the critical points and to increase the hysteresis. This has been carefully analyzed and discussed by Meyer³ who states that 0.10 per cent. manganese lowers Ar_3 by about 5°C., Ar_3 being lower by 60° in a 1 per cent. manganese steel.

The effect of manganese on Ar_1 can be seen from Table 39 taken from Stead's work.⁴

TABLE 39.— Ac_1 AND Ar_1 CRITICAL POINTS OF STEEL

C	Mn	S, P, etc.	Ac_1 (Brayshaw), ⁵ °C.	Ac_1 (Stead), ⁶ °C.	Ac_1 (Hadfield), ⁷ °C.	Ar_1 (Hadfield), ⁷ °C.
0.88	0.06	very low	727	729	731	708
0.88	0.50	very low	726	727
0.89	0.94	very low	722	723
1.00	2.04	very low	713	715	715	667

Howe⁸ states that manganese lowers Ar_1 and Ar_3 at a rate which for Ar_1 is between 24° and 50° for 1 per cent. manganese. It at times raises and at times lowers Ac_1 and Ac_3 .

The influence of gases on the critical points has been studied by Andrew⁹ who concludes that the removal of gases by heating *in vacuo* at temperatures up to 1000°C. has no appreciable effect on the critical points, but he observes that the Ar_3 point of

¹ GUTOWSKY, *Metallurgie*, 1909, Vol. 6, p. 731; WARK, *Ibid.*, 1911, Vol. 8, p. 104; and SALDAU and GOERENS, *Journ. Russ. Met. Soc.*, 1914, p. 789.

² TSCHISCHEWSKY and SCHULGIN, *Journ. Iron and Steel Inst.*, 1917, No. 1, p. 189.

³ *Stahl u. Eisen*, 1914, Vol. 34, p. 1395.

⁴ *Loc. cit.*

⁵ Brayshaw; micrographic method.

⁶ Stead: differential heating.

⁷ Hadfield: thermal analysis.

⁸ *Trans. Amer. Inst. Min. Eng.*, 1913, Vol. 47, p. 740.

⁹ *Iron and Steel Inst. Carn. Sch. Mem.*, 1911, Vol. 3, p. 236.

wrought iron was lowered about 19°C. and the Ar₁ point of the 0.50 per cent. carbon steel was raised 16°C. Heating iron and steel in ammonia gas produces marked changes due to the absorption of nitrogen and hydrogen. Burgess and Crowe remark that gases are not sufficiently eliminated even by several heatings to 1050°C. *in vacuo* and that the samples should be melted *in vacuo*. They found a hysteresis of 20 to 40°C. of the A₃ point in pure iron containing gas, whereas the normal hysteresis (in remelted iron) is 10 to 14°C. In control work for technical heat treating, the critical point specimens should be in the same condition as the material to be treated.

The equilibrium temperatures, Ae₃ and Ae₁, have been discussed at length by Howe.¹ The two branches of the A₃ curves as determined by a weighted average of the more important determinations can be expressed by the formulæ

$$T^{\circ} = 917^{\circ} - 306 \times C, \text{ for G-O in Fig. 53}$$

$$T^{\circ} = 820^{\circ} - 105.5 \times C, \text{ for O-S in Fig. 53}$$

where C equals carbon in per cent. and T° equals the temperature for Ae₃. Ae₁ was given as probably between 715° and 723° but more probably at 723°. This latter value agrees very well with the results of Ruer and Goerens² who gave as the mean of Ac₁ and Ar₁, or "equilibrium" temperature, 721°C. The value of 917°C. for pure iron is too high, according to the work of Burgess and Crowe and might better be assumed to be 900°C.

The effect of the maximum heating temperature on the "lag" on cooling must be allowed for in critical point determinations (of the Ar points) and it is well to assume a constant practice such as heating at a definite and known rate to a specified maximum temperature, such as 900° or 950°C. for a definite length of time, and then cooling at a definite rate. Only in this way can uniform results be secured.³ Fortunately, as has been pointed out, the Ac points are not affected by the previous maximum heating temperature and uniform practice can be secured by maintaining a reasonably constant rate of heating.⁴

¹ *Loc. cit.*, pages 1067 and 1093.

² *Ferrum*, 1917, Vol. 14, p. 161.

³ For a discussion of this subject, see HOWE, *Trans. Amer. Inst. Min. Eng.*, 1913, Vol. 47, p. 740.

⁴ It is conceivable that a coarse structure in which the ferrite occurs as large polygonal grains may give high values for the Ac₃ point, but even here the Ac₃ point determined would give the correct minimum temperature for the correct quenching or grain refining of a steel in such a condition.

The Properties of Heat Treated Steel: *Mild Steel*.—Arnold reports that quenching in iced brine from about 890°C. increased the tensile strength of iron to 72,500 lbs. Charpy, using a mild steel containing 0.07 per cent. carbon, 0.01 per cent. silicon, 0.01 per cent. manganese, 0.01 per cent. sulphur and a trace of phosphorus obtained the following results.

TABLE 30.—EFFECT OF WATER-QUENCHING ON PROPERTIES OF NEARLY PURE IRON

Quenching temperature, °C.	Elastic limit, lb. per sq. in.	Tensile strength, lb. per sq. in.	Elongation, per cent.	R. A., per cent.
20	29,868	41,245	40.4	76.0
700	41,101	46,900	41.0	74.3
900	56,000	76,080	20.2	69.8

A short time ago the writer had a number of one-half inch bars of Armco iron quenched from temperatures above A_c_3 and tested in the tensile testing machine. In no case was there any appreciable difference between the quenched bars and the normal hot-rolled bars. Just recently Hatfield has published figures for wrought iron in various conditions of heat treatment and he too found the properties are quite uniform at about the following values: yield point, 20,000 pounds; tensile strength, 40,000 pounds; elongation, 42 per cent.; and reduction of area, 64 per cent. The fracture was fibrous in all cases. The notched bar impact test showed that the resistance dropped from over 60 foot-pounds to 22 foot-pounds when the wrought iron was quenched from 770°C. or above and that the fracture changed from the normal fibrous character to a coarsely crystalline fracture.

Nead¹ has recently determined the effect of quenching on low carbon steels as shown in Table 41.

Pomp,² using a very pure material (C 0.08 per cent., Si 0.02 per cent., Mn 0.07 per cent., P 0.01 per cent., S 0.002 per cent., Cu 0.04 per cent.), determined the effect of heat treatment on the notch toughness and Brinell hardness. His results are summed up in Table 42.

¹ *Trans. Amer. Inst. Min. Eng.*, 1916, Vol. 53, p. 218. The annealing and quenching temperatures are those recommended by the A. S. T. M.

² *Ferrum*, 1916, Vol. 13, p. 49.

TABLE 41.—PROPERTIES OF HEAT-TREATED MILD STEEL

Composition		Treatment	Y. P., lb. per sq. in.	T. S., lb. per sq. in.	Elonga- tion, per cent. 2 in.	R. A., per cent.	Brinell hardness
C	Mn						
0.14	0.45	Hot rolled.....	45,000	59,500	37.5	67.0	112
0.14	0.45	Annealed.....	31,000	54,500	39.5	67.0	107
0.14	0.45	Quenched H ₂ O.....	90,000	21.0	67.0	170
0.14	0.45	Quenched oil.....	56,500	71,500	34.0	75.5	134
0.18	0.56	Hot rolled.....	45,000	63,000	36.0	67.0	118
0.18	0.56	Annealed.....	39,500	59,000	36.5	67.0	111
0.18	0.56	Quenched H ₂ O.....	105,000	16.5	57.2	228
0.18	0.56	Quenched oil.....	54,500	78,700	31.0	75.2	156

TABLE 42.—TOUGHNESS AND HARDNESS OF HEAT-TREATED MILD STEEL

Property	Untreated (hot rolled)	Quenched in water (18°) after annealing					
		At 800°		At 1000°		At 1300°	
		1 hr.	8 hrs.	1 hr.	8 hrs.	1 hr.	8 hrs.
Notch toughness, mkg. per sq. cm.....	45.8	50.2	47.8	52.8	47.2	17.2	7.3
Brinell hardness.....	98	150	156	178	173	231	235

Results are average values of two bars.

In technical practice the most important heat treatment of mild steel (wire, sheets, plate, etc.) is annealing to soften the material and remove internal strains, non-uniformities, etc. Care must be taken during the annealing operations lest the material become brittle. This subject has been studied by various authorities among whom may be mentioned Stead,¹ Ridsdale,² Heyn,³ and Pomp.⁴

Pomp found that annealing up to eight hours at 800° produced a marked increase in the notch toughness although the grain size was increased somewhat, and that annealing up to 1000°

¹ "On the Crystalline Structure of Iron and Steel," *Journ. Iron and Steel Inst.*, 1898, No. 1, p. 145.

² "Brittleness in Soft Steel," *Journ. Iron and Steel Inst.*, 1898, No. 1, p. 220, "Practical Microscopic Analysis," *Ibid.*, 1899, No. 2, p. 102; "The Correct Treatment of Steel," *Ibid.*, 1901, No. 2, p. 52.

³ "On the Overheating of Mild Steel," *Journ. Iron and Steel Inst.*, 1902, No. 2, p. 73.

⁴ *Loc. cit.*

for short periods caused no deterioration. His results may be summarized as follows.

TABLE 43.—EFFECT OF ANNEALING MILD STEEL

	Original material	8 hrs. at 800°C.	8 hrs. at 1100°C.	8 hrs. at 1200°C.
Grain size, μ^2	315	715	1480	16,090
Notch toughness, mkg. per sq. cm.....	45.8	58.8	33.2	5.8
Brinell hardness.....	98	92	85	83

Chemical Analysis: C 0.08, Si 0.02, Mn 0.07, P 0.01, S 0.002, Cu 0.04.

To produce the lowest notch toughness (5 mkg./sq. cm.), which corresponded to a very brittle and coarse grained material, it was necessary to anneal one hour at 1300°, two hours at 1200°, or thirty-eight hours at 1100°. According to this work, the most suitable annealing temperature for this material is from 600° to 800° which can be maintained for hours without injuring the material. This is confirmed by the work of Stadeler who found that one and one-half hours annealing at 860°C. \pm 10°C. was sufficient to give the maximum notch toughness in $\frac{3}{4}$ inch open hearth plate, carbon = 0.1 per cent.¹

These figures would hardly apply to the ordinary commercial grades of steel which contain greater amounts of impurities, *i.e.*, ordinary mild steel would deteriorate more rapidly than the material used by Pomp.

Joisten² concluded that the growth in grain size with annealing temperature increased to a maximum at 700°C. above which it again fell off.

Restoration of Overheated Steel.—Heyn, confirming the work of Stead, reported on annealing (reheating) to remove brittleness due to overheating mild steel. First of all, mild steel can be made brittle by heating above some temperature, said to be between 900° and 1100°C. the brittleness increasing with both time and temperature. Several hours at 1100° to 1200°C. is sufficient to "overheat" the steel. This effect can be remedied by reheating to just above A_{c_4} for half an hour, or by reheating to just below A_{c_3} for a considerably longer period, at least several days. In

¹ *Ferrum*, 1914, Vol. 11, p 271.

² Intern. Congress for Mining and Metallurgy, Dusseldorf, 1910.

this work the "bending number" was used as a measure of the toughness of the material¹ which is 0 to $\frac{1}{2}$ for overheated steel, $3\frac{1}{2}$ for ordinary rolled steel and 4 for annealed steel.² The steel experimented with was very pure and analyzed carbon 0.07 per cent., manganese 0.10 per cent., silicon 0.06 per cent., phosphorus 0.01 per cent., sulphur 0.02 per cent. and copper 0.15 per cent.

The restoration of overheated steel (two hours at 1300°C.) was also studied by Pomp whose results follow.

TABLE 44.—RESTORATION OF OVERHEATED MILD STEEL

	Reheating: Time and temperature						
	at 850°	at 900°			at 1100°		
	8 hrs.	$\frac{1}{4}$ hr.	1 hr.	8 hrs.	$\frac{1}{4}$ hr.	1 hr.	8 hrs.
Charpy test mkg	5.8	40.2	59.5	56.6	41.5	43.6	27.0

Brittleness due to overheating can be distinguished from that due to cold working or working at blue heat or to quenching, by the considerably higher temperature and longer time required for its removal.

Microscopic Characteristics of Overheated Steel.—Heyn reports that "there exists no assured microscopic characteristics by which the overheating of mild steel might be detected."³ But it is reasonable to assume that in general practice coarse grained material is comparatively brittle while fine grained material is comparatively tough, and Stead in particular noted a coarse ferrite structure in brittle steel. However, it was shown by Heyn that a coarse structure (several days at 700 to 900°C.) could have the maximum toughness (B. N. = $3\frac{1}{2}$) and that mild steel when heated to 1450°C. and quenched in water could be fine grained

¹ B. N. was taken as the number of times a notched bar could be bent backwards 90° and then forwards 90°, each 90° bending being one bend. For brittle steels, B. N. is under 1; for tough materials, B. N. = 3 to 4.

² It is interesting in this connection that reheating to 1100° for a short time will also remove the brittleness. Copper, made brittle by overheating, cannot be restored by heating alone; mechanical working is required. The difference in the behavior of iron and copper, in this respect, is due to the polymorphic transformation in iron. As RIDSDALE points out, bad forms of brittleness in mild steel can hardly be restored by heating alone. Welded joints, therefore, should preferably be forged but even a simple reheating to 900°-1000° would improve their properties.

³ *Loc. cit.*, p. 100.

but comparatively brittle ($B. N. = 1\frac{1}{2}$). A fine grained structure produced by hot work and a coarse grained structure produced by overheating, confirm the general relationship supposed to exist between grain size and brittleness.

Stead noted a peculiar brittleness, known as "rectangular brittleness," which is found only in annealed sheets from 10 to 18 gage and containing about 0.05 per cent. carbon. This brittleness caused a peculiar fracturing at 90° if the sheet were struck a sharp blow. The edges of the fracture always ran at 45° to the direction of rolling. The fractures running through adjacent crystals were seen to be continuous, which led to the assumption that the crystals were similarly oriented and that therefore the "brittleness was due to the symmetrical orientation of the crystals in contiguous granules." This brittleness was removed by reheating to 900° which was supposed to orient the crystals in a haphazard fashion. Heyn showed by means of "deep etching" that brittleness of coarse grained ferrite at least is not necessarily due to continuous orientation and is inclined to discredit the above theory. It transpired in the course of the discussion that sheets exhibiting rectangular brittleness were high in phosphorus so that it is undoubtedly true that this brittleness is different from that due to overheating.

Medium-Carbon Steel.—The properties of forged steel, both plain and heat treated, have been repeatedly reported¹ and are now practically a matter of common knowledge. The aim of heat treatment, here, is to produce in the steel the best combination of strength, ductility and toughness of which the particular steel is capable and which is compatible with the other considerations, such as cost, design of the part, etc. In terms of the microconstituents, this means the production of sorbite. Three different methods of treatment are generally practiced. If the very best properties (maximum grain refinement) are required, the steel should be quenched from above A_{c3} rapidly enough to suppress the segregation of ferrite. This treatment results in a structure which is either martensite or martensite plus troostite.

¹ The work which stands out as a classic in this field is the Sixth Report to the Alloys Research Committee, commenced by ROBERTS-AUSTEN and completed by W. GOWLAND. This paper deals very thoroughly with the tensile results and microstructure of a series of steels varying in carbon from 0.13 per cent. to 1.3 per cent., and subjected to quite a wide range of heat treatment. Other important results have been reported by WAHLBERG, McWILLIAM and BARNES, HANEMANN, MARS, MILLS, and others.

The steel in this condition is then reheated (tempered) to some temperature above 400°C. and below 650°C., which treatment, properly carried out, produces a fine grained and uniform sorbite which has a very high notch toughness and the desired strength and ductility. (See Fig. 69.) Tempering between 650°C. and A_{c1} produces granular pearlite, which while possessing ductility, does not have sufficient toughness, particularly when tested in the notched condition.¹ A second means of producing sorbite

TABLE 45.—MECHANICAL PROPERTIES OF HEAT-TREATED MEDIUM-CARBON STEEL

Composition		Treatment	Y. P., lb. per sq. in.	T. S., lb. per sq. in.	Elonga- tion, per cent. 2 in.	R. A., per cent.	Brinell hard- ness
C	Mn						
0.32	0.51	Hot rolled.....	49,500	75,500	30.0	51.9	144
		Annealed.....	41,000	70,000	30.5	51.9	131
		Quenched in H ₂ O.....		135,000	8.0	16.9	255
		Quenched in oil.....	67,500	101,000	23.5	62.3	207
		Oil: Tempered at 650°....	61,500	84,000	30.0	71.4	163
0.46	0.40	Hot rolled.....	52,500	86,500	22.5	30.7	160
		Annealed.....	48,000	79,500	28.5	46.2	153
		Quenched in H ₂ O.....		220,000	1.0	0.0	600
		Quenched in oil.....	87,500	126,500	20.5	51.9	255
		Oil: Tempered at 560°....	81,500	111,500	24.0	57.2	202
0.57	0.65	Oil: Tempered at 650°....	73,000	98,000	25.5	59.8	192
		Hot rolled.....	57,000	106,500	19.0	27.4	220
		Annealed.....	50,000	95,000	25.0	40.3	183
		Quenched in H ₂ O.....		215,000	0.0	0.0	578
		Quenched in oil.....	105,000	152,000	16.5	40.3	311
0.71	0.67	Oil: Tempered at 460°....	97,500	145,000	16.0	46.2	293
		Oil: Tempered at 650°....	79,500	113,000	24.0	62.3	228
		Hot rolled.....	66,000	128,000	15.0	20.5	240
		Annealed.....	46,500	111,500	16.5	24.0	217
		Quenched in oil.....	100,000	184,500	1.5	0.0	364
		Oil: Tempered at 460°....	115,500	177,000	10.0	34.0	340
		Oil: Tempered at 560°....	106,000	148,500	17.0	48.0	311
		Oil: Tempered at 650°....	91,000	125,500	19.5	57.2	269

Quenching and annealing temperatures are those recommended by the American Society for Testing Materials.

¹ Failure to observe this point may lead to a weakness in the part which is not detected by the usual physical tests nor by microscopic examination unless the lens used is high powered and with good optical correction. It is certain that an examination at $\times 100$ does not bring out the difference between sorbite and ordinary granular pearlite. A valuable control test for use here is the notched bar impact test which might be profitably supplemented by a fatigue test on notched bars.

FORGING STEEL—0.40 PER CENT. CARBON
 Quenched in water from 1450°F. or 790°C.

Drawn at	Y. P., lb. per sq. in.	T. S., lb. per sq. in.	Elong., per cent. 2 in.	R. A., per cent.	Brinell hardness
315°C.— 600°F.	175,000	200,000	7.5	28	385
430°C.— 800°F.	130,000	155,000	15	45	335
540°C.—1000°F.	95,000	120,000	20	54	285
650°C.—1200°F.	70,000	100,000	25	62	235

FORGING STEEL—0.40 PER CENT. CARBON
 Quenched in oil from 1500°F. or 815°C.

Drawn at	Y. P., lb. per sq. in.	T. S., lb. per sq. in.	Elong., per cent. 2 in.	R. A., per cent.	Brinell hardness
315°C.— 600°F.	87,000	125,000	16	55	230
430°C.— 800°F.	82,000	118,000	18	56.5	216
540°C.—1000°F.	71,000	110,000	22	58	210
650°C.—1200°F.	62,000	95,000	25	64	196

is to quench the steel in oil from above Ac_3 . This treatment gives a structure as shown in Fig. 70, already described. It is not as expensive as the double treatment and is sufficient for many purposes. Finally, the oil treatment is often followed by a draw below Ac_1 . This treatment eliminates internal strains and serves to produce the desired properties.

Table 45, first part, gives the properties of heat treated steel as reported by Nead. In the second part are given the properties of a forging steel with 0.40 per cent. carbon in about one inch sections.

High-Carbon Steel.—High-carbon steels are commercially important in a heat treated condition largely on account of (1) their hardness, giving them cutting ability or resistance to abrasion, or (2) their high elastic limit, which makes them useful as springs. To secure these properties it is necessary to heat treat the steel very carefully.

Spring Steel.—The valuable property of spring steel is its ability to deform under a load and to return to its original shape on release of the load. The value of a steel for spring purposes is determined largely by its resiliency and its ability to absorb a heavy impact without suffering permanent deformation. The carbon content varies from 0.85 to 1.15, increasing in amount as

the severity of the service increases, with manganese under 0.50 to avoid too great brittleness. The heat treatment is selected to give a high elastic limit with a fair amount of ductility, the latter to avoid undue brittleness. This is secured by quenching the steels from 750° in water or oil, as the case may be, and tempering at temperatures up to 400° to produce troostite. Table 46 gives examples of the properties of spring steel, according to Nead.

TABLE 46.—MECHANICAL PROPERTIES OF HEAT-TREATED HIGH-CARBON STEEL

Composition		Treatment	Y. P., lb. per sq. in.	T. S., lb. per sq. in.	Elong., per cent. 2 in.	R. A., per cent.	Brinell hard- ness
C	Mn						
0.83	0.55	Hot rolled.....	70,500	139,000	12.5	13.3	269
		Annealed.....	50,500	114,000	15.0	20.5	223
		Quenched in H ₂ O.....	93,000	184,000	0.0	0.0	744
		Quenched in oil.....	138,000	184,000	4.0	5.7	418
		Oil: Tempered at 375°.....	134,000	198,000	11.5	34.0	364
		Oil: Tempered at 460°.....	134,000	194,000	14.0	37.2	387
		Oil: Tempered at 650°.....	97,500	129,000	19.0	46.2	277
1.01	0.39	Hot rolled.....	86,000	152,000	9.5	13.3	302
		Annealed.....	53,800	99,400	24.0	36.2	192
		Quenched in H ₂ O.....	153,000	192,000	0.0	0.0	578
		Quenched in oil.....	127,000	192,500	10.5	34.0	387
		Oil: Tempered at 375°.....	127,500	195,000	12.5	34.0	375
		Oil: Tempered at 560°.....	104,500	168,500	14.5	30.7	321
		Oil: Tempered at 650°.....	86,000	134,000	20.0	40.3	277

Tests of spring steel for locomotives are given in the following table.¹ The determinations were made from transverse tests

TABLE 47.—TESTS OF SPRING STEEL.

Treatment	Elastic limit, lb. per sq. in.	Deflection
Annealed at 760°.....	78,500	Not broken at 1.1 in.
Quenched in oil at 790°, tempered at 290°.....	137,500	Not broken at 1.1 in.(a)
Quenched in oil at 790°, tempered at 260°.....	160,500	Not broken at 1.1 in.(a)
Quenched in oil at 790°, tempered at 200°.....	177,500	Not broken at 1.1 in.(a)
Quenched in oil at 790°.....	187,500	Not broken at 1.1 in.
Quenched in water at 775°, tempered at 565°.....	180,500	Not broken at 1.1 in.
Quenched in water at 775°, tempered at 480°.....	234,000	Not broken at 1.1 in.
Quenched in water at 775°, tempered at 400°.....	240,800	0.744 in.
Quenched in water at 775°, tempered at 315°.....	219,800	0.175 in.
Quenched in water at 775°.....	212,000	0.171 in.

Modulus of elasticity remained constant at 29-30,000,000 lb. per sq. in.

(a) Cited as customary shop practice for producing "spring temper."

¹ FRY, Int. Soc. Test. Materials, 1909, 1, 3.

of twelve-inch bars loaded at the middle point. The steel tested contained 1.01 per cent. carbon and 0.38 per cent. manganese.

Tool Steel and Cullery Steel.—The high carbon steels are used for purposes which require cutting hardness. The heat treat-

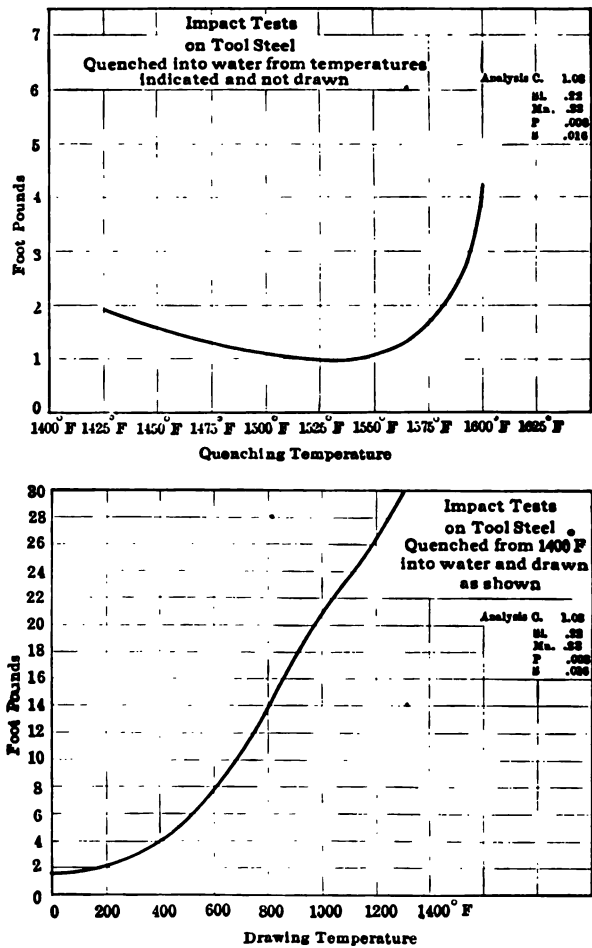


FIG. 82.—Effect of quenching temperature and drawing temperature on the impact figure of tool steel. (Stagg.)

ment used is one which will produce martensite or hardenite, followed, usually, by a draw to produce troostite, which, while diminishing the hardness somewhat, gives the required amount of toughness. The effect of quenching temperature and drawing

temperature on the resistance to impact, according to Stagg is shown in Fig. 82. In case brittleness is entirely secondary to the cutting properties the steel usually contains excess cementite and is heat treated to produce a ground mass of hardenite. This structure in a razor blade is shown in Fig. 83.

Effect of Drawing Time.—It has already been shown that the nature of the change in quenched steel when reheated is that of a substance tending to change from a metastable condition to a stable condition. Consequently the change does not depend on any particular temperature but is one which proceeds further the higher the temperature and the greater the length of time



×1250

FIG. 83.—Properly forged and hardened razor blade. Cementite in structureless martensite (hardenite). (Hanemann.)

allowed.¹ Hanemann has shown that the velocity of the change increases rapidly as the drawing temperature is raised and that only a few seconds are required for its completion at 650°C.² The velocity of the change also decreases as the change proceeds. Thus it is that the time which quenched steel is held at the drawing temperature has its effect on the final properties of the steel. In one case the difference between eight minutes and forty minutes at 800°F. (427°C.) was sufficient to lower the Brinell

¹ Early work in this field which promises to be of considerable importance is that of STROUHAL and BARUS.

² *Stahl u. Eisen*, 1911, Vol. 31, p. 1365.

hardness from 425 to 340.¹ According to Hayward and Raymond, the effect of time at temperatures up to 500°C. is negligible while at higher temperatures it is still small, although noticeable. Their steel contained 0.45 per cent. carbon, 0.56 per cent. manganese and 0.016 per cent. phosphorus.²

Relation Between the Hardness of Steel and Its Strength.—The Brinell hardness test furnishes an indication of the tensile strength of carbon steel. This relationship has been established by various investigators, notably Wahlberg,³ H. Le Chatelier,⁴ Grard,⁵ Devries,⁶ Abbot,⁷ and McWilliams and Barnes.⁸ The results obtained by Grard expressed as

$$\frac{\text{Tensile strength}}{\text{Brinell hardness number}} = K$$

may be given as follows.

TABLE 48.—RELATION BETWEEN BRINELL HARDNESS AND TENSILE STRENGTH
For Annealed Steel

Steel	Tensile strength, lb. per sq. in.	Brinell hardness no.	Ratio K
Extra mild steel.....	48,300– 56,800	Below 120	510
Mild steel.....	56,800– 64,000	120–160	500
Medium hard steel.....	75,000– 92,000	160–180	500
Hard steel.....	92,000–106,600	Above 180	495

For Quenched and Tempered Steel

Steel	Tensile strength, lb. per sq. in.	Brinell hardness no.	Ratio K
Mild steel.....			
Medium hard steel.....	Above 85,000	Above 250	480
Hard steel.....	Above 99,500	Above 275	450

¹ MATTHEWS and STAGG, *Trans. Amer. Soc. Mech. Eng.*, 1914, Vol. 35. This question will be dealt with at greater length in Pt. III.

² *Trans. Amer. Inst. Min. Eng.*, 1917, Vol. 56, p. 517. This effect has also been studied by HOWE and LEVY—*Proc. Amer. Soc. Test. Mat.*, 1916, Vol. 16, Pt. II, p. 7—whose results will be considered at another place.

³ *Journ. Iron and Steel Inst.*, 1901, No. 1, p. 243; 1901, No. 2, p. 234.

⁴ *Rev. de Metallurgie*, 1906, Vol. 3, p. 689.

⁵ *Proc. 6th Congress Intern. Soc. Test. Mater.*, N. Y. City, 1912, Paper III.

⁶ *Ibid.*, Paper IX.

⁷ *Trans. Amer. Soc. Test. Materials.*

⁸ *Journ. Iron and Steel Inst.*, 1915, No. 1, p. 125.

The value and utility of Brinell and scleroscope determinations, when used as a measure of the tensile strength, have been considered in Chapter VII, Part I. At that place it was shown that the hardness: tensile strength relationship is but an approximate one.¹ It might perhaps be further pointed out that it is only the tensile strength and not the elastic limit which bears a direct relationship to the hardness number, so that in the inspection of materials whose elastic limit is of prime importance, such as shells, the Brinell test could be used only when all pieces are of the same material, have been treated in the same manner and have practically the same properties. Under other conditions, when the coördination of the elastic limit and the tensile strength was not determined or could not be relied upon, the Brinell test,

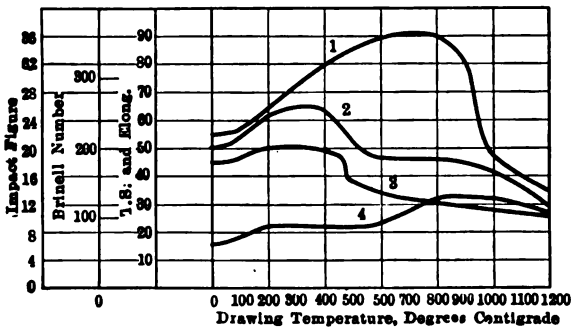


FIG. 84.—Effect of drawing temperature on the properties of "soft steel." (Grard.)

1. Notched bar impact figure in MKg./sq. cm. Frémont test.
2. Tensile strength in Kg./sq. mm.
3. Brinell hardness.
4. Elongation in per cent.

obviously, could not be used, inasmuch as the elastic limit is the property of vital importance and not the tensile strength.

The Modulus of Elasticity.—The modulus of elasticity remains practically constant for carbon steel at 2.9 to 3×10^7 pounds per square inch, it being very little affected by heat and mechanical treatment. It is on this account that "stiffness" frequently must be secured through design of the part rather than by heat treatment.

¹ The author has in his private notes the results of a series of steels which show a variation in K as follows. For low carbon steel, K varies with the heat treatment from 520 to 580; for medium carbon steel, from 480 to 540; and for high carbon steel, from 500 to 540.

Ductility as Measured by the Bend Test.—A very important technical test, to bring out the ductility of material, is the bend test, either hot or cold. The test piece is either bent back flat on itself or around a spindle having a certain specified diameter. The material is supposed to bend in this manner without developing cracks on the outer fibers. This test, as applied to structural material is given in Table 35.

Impact Resistance of Steel.—There has been a great deal of literature on the resistance of notched bars to impact, but there

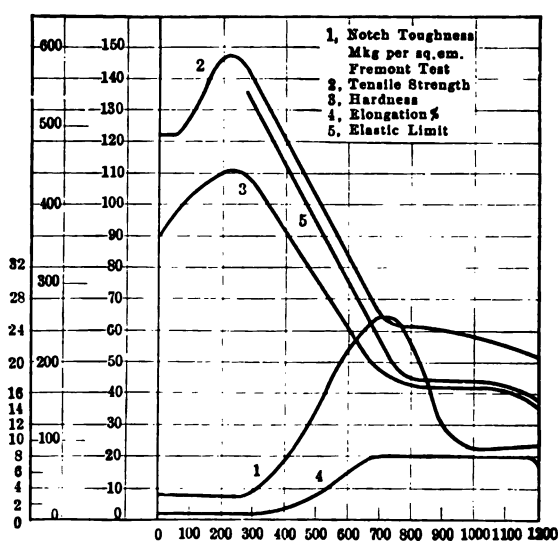


FIG. 85.—Effect of drawing temperature on the properties of "semi-hard steel." (Grard.) Same scales as in Fig. 84.

is as yet no work available which gives us all the desirable information on this subject. This is due principally to the lack of generally accepted methods for this kind of testing in spite of the favorable progress made by the Charpy method. In the following figures, values for the notch toughness, hardness and tensile properties of three different grades of steel, as determined by Grard, are given. The ordinates represent values of the properties, and the abscissae drawing or reheating temperatures.

In Table 49 are given results obtained by Philpot.

TABLE 49.—NOTCH TOUGHNESS OF MILD STEEL

Test	Composition					Lb. per sq. in.		Elong., per cent.	R. A., per cent.	R. I., ft.-lb.
	C	Si	Mn	S	P	Y. P.	T. S.			
<i>C</i>	0.20	0.20	0.77	0.054	0.054	62,720	87,500	30.5	54.6	89.2
<i>D</i>	0.24	0.11	0.82	0.027	0.018	80,640	82,880	24.0	59.2	12.0
<i>G</i>	0.20	0.20	0.76	0.054	0.054	56,448	86,200	33.0	56.0	79.3
<i>H</i>	0.24	0.11	0.82	0.027	0.018	80,640	83,776	22.5	58.0	9.6

C and *G*, Commercial heat treatment; *D*, untreated; *H*, untreated.

Elongation measured on two inches.

R. I.—Determinations made with the Isod machine; the values are in ft.-lb. The notch was 45°, 2 mm. deep, with a radius at the bottom of 0.25 mm.

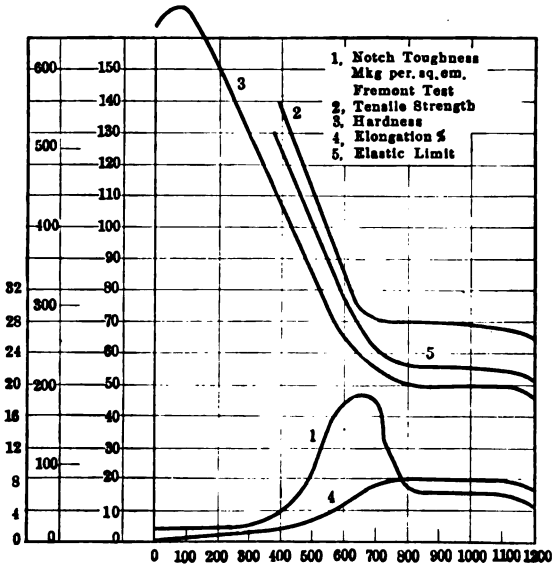


FIG. 86.—Effect of drawing temperature on the properties of "hard steel." (Grard.) Same scales as in Fig. 84.

Resistance of Steel to Alternating or Vibratory Stresses.—

A very extensive series of tests on the resistance of steels of different carbon contents to alternating stresses has been carried out at the Watertown arsenal. Reports on these tests are contained in the Tests of Metals for 1903–1909. Certain of these results are reproduced in Table 50 and show that the vibratory strength of steel increases very considerably as the carbon increases.

TABLE 50.—ENDURANCE TESTS OF STEEL. WATERTOWN ARSENAL

Carbon, per cent.	Elastic limit, Lbs. per sq. in.	Repetitions
0.17	51,000	20,000
0.34	54,000	65,000
0.55	59,000	95,000
0.73	64,000	230,000
0.82	64,000	215,000
1.09	77,000	60,000

Material tested—hot rolled bars.

Fibre stress varied from -50,000 to +50,000 lbs. per sq. in.

These figures indicate that the vibratory strength of steel increases as the grain size decreases and the same principle undoubtedly holds for steel in the heat treated state so that it can be safely assumed that a sorbitic or troostitic structure is superior to the annealed structure. This has been brought out by Roos of Hjelmsäter as can be seen from Table 51. The heat treatment of high carbon steel so as to give a high elastic limit or a troostitic structure is further confirmation of this point.

TABLE 51.—EFFECT OF HEAT TREATMENT ON THE VIBRATORY STRENGTH HJELMSÄTER

Material	Prop. limit, Lbs. per sq. in.	T. S. lbs. per sq. in.	Elongation on 10 diam. per cent	Endurance Limit
R—annealed.....	33,000	50,000	34.1	23,000
S—annealed.....	50,500	83,000	23.8	31,000
S—oil quenched.....	70,500	110,000	15.6	40,000
T—annealed.....	51,000	116,000	14.3	35,500
T—oil quenched.....	94,500	151,000	11.0	54,000

Endurance limit = fibre stress in lbs. per sq. in. for 1,000,000 repetitions.
Stress varied from 0 to +.

	C	Si	Mn	P	S
R	0.11	0.01	0.33	0.019	0.013
S	0.40	0.20	0.51	0.027	0.011
T	0.65	0.20	0.49	0.023	0.007

Sixth Cong. Intern. Soc. Test. Mat., New York, 1912, Paper 5, 11-b.

Prof. Smith has also studied the variation in the limiting range with the carbon content and has shown that the limiting range runs parallel to the yield point. His results are shown in Fig.

The influences which affect the yield point, such as mechanical work (?), heat treatment, etc., have the same effect on the limiting range. In this way, over-annealing, by lowering the yield point, can lead to a premature failure as a consequence of the lowering of the limiting range.¹

Nusbaumer, in a report on dynamic tests on steel,² summarizes as follows:

"(a) In the annealed state (normalized): The resistance to rotary bending stresses, to repeated shocks, or to alternating bending (vibrations) is proportional to the percentage of carbon in steels containing carbon lower than 0.25 to 0.35 per cent. Above this percentage the ratio between the percentage of carbon and the resistance becomes inverse as regards repeated shocks, but remains as it was in regard to rotary bending and alternating bending (vibrations).

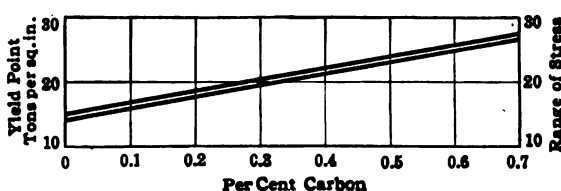


FIG. 87.—Effect of carbon content of steel on the resistance to fatigue. (Smith.) Upper line, range for 10^6 alternations for mean stress = $\frac{1}{2}$ maximum stress. Lower line, yield point in the tensile test.

"(b) Quenching, followed by annealing, raises the resistance. . . . to repeated shocks and to alternating bending.

"(c) Quenching (not followed by annealing) raises the resistance of mild carbon steels to repeated shocks. . . . and diminishes considerably the resistance of plain carbon steels to alternating bending (vibrations).

"2. No matter what description of repeated stresses a metal may be subjected to, it displays a better resistance thereto, in proportion, other things being equal, as it displays resistance to the simple impact test for notched bars (the Frémont test)."

Summary.—Eliminating the effects of corrosion and mechanical wear, we may say that steels used for construction purposes are rarely known to fail because their tensile strengths are below

¹ Elastic hysteresis, while seldom considered, is known to exist and has been measured thermally (mild steel) by HOPKINSON and WILLIAMS, *Proc. Roy. Soc.*, 1912, Series A, Vol. 87, p. 502. See also ROWETT, *Ibid.*, 1913, Series A, Vol. 89, p. 528.

² Iron and Steel Inst., *Carn. Sch. Mem.*, 1914, Vol. 6, p. 166.

the normal working loads. It is true that abnormal conditions can impose loads on certain members sufficient to cause simple static rupture and it is in such cases that the ductility and toughness act as a factor of insurance to reduce the hazard from the failure of the part. In most cases failures occur because the stresses imposed on the part, even though calculated to be below the danger point, produce strains at some point which are too great for the material to stand continuously. Generally we may say that the failures are due to the notch effect, occasionally to simple fatigue and quite commonly to a combination of these two effects. Thus it is that the important points here are that the steel should have high static strength (elastic limit) to resist the normal and vibratory stresses, and high notch toughness, to give proper security against premature failure. Of these two properties particular attention should be paid to the notch toughness because (a) the elastic limit is easily measured and controlled while (b) the notch toughness is apt to be abnormally low without such being suspected from the elongation and reduction of area from the tensile test. Of equally great importance from the engineer's point of view, are the design and manufacture of the part inasmuch as they should be so controlled that the notch effect and deficiency in notch toughness will lead to a minimum hazard.

We may now consider the requirements which good metallurgical practice would impose on the engineering use and treatment of the medium-carbon or forging steels.

1. The design and service of the part should equalize the strain distribution so that each fibre shall receive only its proportionate share of the total stress. It is known that sudden changes in the cross section produce local and abnormally high strains which are particularly injurious to certain types of structures. The danger due to the presence of such notches, for a given load, increases with increase in the number of repetitions of the load which the part must sustain. Hence some parts are injured even by fine scratches, and rough machine marks are known to have caused premature failure in automobile parts.

2. The part should be heat treated to give a high elastic limit yet not so high that the ductility will be sacrificed. In case the strains are simple fatiguing strains the elastic limit can be made considerably higher, as in the case of springs. The high elastic limit offers the guarantee that the part will have adequate

resistance for the simple static load and for the vibratory stresses, as the factor of safety used reduces the working stresses well below the elastic limit.

3. The part should be heat treated to give reasonably high values for the elongation and reduction of area in the tensile test. This is to guard against the danger from the sudden application of a load in excess of the elastic limit of the part.

4. The part should be heat treated to give high resistance when in a notched condition, to a single load or to repeated loads. This is to minimize the chances of failure in service due to an excessively non-uniform strain distribution. The importance of this factor can hardly be too greatly emphasized on account of the large percentage of failures which can be traced to this source. The mechanism of the failure, in such cases, seems to be a combination of the notch effect and vibratory stresses so that the simple and convenient means of testing the quality of the material would be by the tensile test and the Charpy test. The alternating stress test alone would give equally vague results as the tensile test alone while an alternating stress test on notched bars remains to be developed. At any rate the Charpy test would undoubtedly lead to the same judgment of the material.

5. It is significant to note that the heat treatment to satisfy these requirements is one which produces sorbite, the most valuable structure for the forging steels. From the point of view of the tensile test or simple static strength it would not be necessary to produce sorbite because an annealed steel, while weaker, could be used in larger cross section to give the same strength to the part. From the point of view of the simple vibratory stress test, a high carbon steel or even a high phosphorus steel, could be used to take advantage of the higher elastic limit. But from the point of view of the service conditions it is necessary to produce a highly resistant structure, which is one possessing high notch toughness. Strength, ductility and resistance to vibratory stresses can be obtained with steels showing a "poor" structure if only the part be made large enough. Under unfavorable service conditions, however, the poor structure can fail by gradual disintegration even though the tensile test shows high elongation and reduction of area. From these considerations it seems apparent that structure is the important point in the heat treatment of forging steel and this structure is sorbite. The next considerations in importance are the strength and notch

toughness but if it is known that the correct structure is obtained we might substitute strength and ductility, although this latter substitution is sound only in case it is known that the structure is satisfactory. While the truth of this assertion may be admitted in so far as it applies to the carbon steels, it should be pointed out that it does not necessarily apply to special steels.

The Effect of Cold Work on Steel.—Two of the most important technical operations performed on mild steel (principally sheets) are stamping, pressing, etc., and subsequent annealing of the cold worked steel. On account of the close relationship between these processes, we shall consider first the effect of cold work on steel and then the effect of annealing cold-worked steel.

Mild steel, when in the soft or annealed state, is capable of sustaining a considerable amount of plastic deformation and is drawn out into wire, pressed and stamped into shape and otherwise worked when "cold." This cold distortion produces a hardening or stiffening of the material which always opposes further distortion, and if carried too far leads to brittleness which can result in internal flaws or even ultimate failure. It is of interest to know the properties produced by different degrees of cold work, the extent to which cold working can be continued and, finally, the best method of annealing to eliminate the ill effects in order that the material can be further worked or be put in suitable condition for use.

TABLE 52

Material	Composition				
	C	Mn	P	S	Si
Wrought iron.....	0.11	0.39	0.128	0.022	0.126
Basic Bessemer steel.....	0.07	0.48	0.080	0.056	0.006
Electric steel.....	0.12	0.56	0.016	0.017	0.148
Electric steel.....	0.27	0.43	0.023	0.015	0.167
Open hearth steel.....	0.55	0.47	0.068	0.036	0.262
Electric steel.....	0.62	0.65	0.045	0.017	0.223
Open hearth steel.....	0.78	0.38	0.016	0.019	0.113
Electric steel.....	0.98	0.43	0.025	0.015	0.158

These questions have been systematically studied by Goerens, whose results will be briefly considered.¹ The first part of the

¹ Iron and Steel Inst., Carn. Sch. *Mem.*, 1911, Vol. 3, p. 320; *Ferrum*, 1912-13, Vol. 10, p. 65.

work is devoted to the effect of cold drawing and cold rolling on steel. The original "untreated" material used was ordinary hot-rolled rod, usually 5.3 mm. in diameter. The compositions were as shown in Table 52.

It was found out, first of all, that the extent to which cold working could be continued decreased as the carbon content increased. Table 53 gives the comparison of wrought iron and steel by giving the properties of the original material and of the same after reduced by drawing by the maximum amount of which the material was capable.

TABLE 53.—EFFECT OF COLD WORK ON THE TENSILE PROPERTIES OF STEEL

Material	Maximum reduction, per cent.	Tensile strength lbs. per sq. in.		Elongation per cent.		R. A., per cent.	
		Original	Max. reduction	Original	Max. reduction	Original	Max. reduction
Steel..... C = 0.07	95.2	59,450-153,700		30.6-5.2		73.0-25.0	
Wrought Fe..... C = 0.11	39.8	59,000-90,300		26.1-3.5		44.7-17.5	
Electric steel..... C = 0.12	70.4	58,700-120,000		32.7-6.0		70.0-30.0	
Electric steel..... C = 0.27	70.4	69,000-136,400		29.9-3.0		59.5-22.7	
O. H. Steel..... C = 0.55	86.5	93,000-202,200		23.3-6.3		38.0-13.4	
Electric steel..... C = 0.62	44.3	115,000-173,500		17.1-2.5		26.1- 6.0	
O. H. steel..... C = 0.78	67.5	115,400-182,000		19.2-6.0		36.0-15.5	
Electric steel..... C = 0.98	28.3	146,500-186,000		6.7-0.3		7.8- 2.5	

This table shows that material when drawn even to the breaking point need not necessarily be brittle, but that it may still retain a certain degree of ductility. On this account it may still be suitable for structural purposes. The modulus of elasticity, as obtained by use of the Martens mirror extensometer, was found to be independent of the degree of cold working.

The tenacity developed by cold working is dependent on the following factors:

1. The capacity of the material for cold working. Thus wire is made considerably stronger than sheet, and electric steel stronger than Bessemer steel.
2. The chemical composition. Discussed above.
3. The original dimensions. See 1.

The sclerometric or scratch hardness, as determined by the Martens sclerometer, was found to be unchanged even by the severest cold working. The Brinell hardness varied considerably with the work done, but the ratio, hardness: tensile strength, varied by as much as 20 per cent. so that it would hardly be

feasible to calculate the strength from the Brinell hardness. Table 54 shows the effect of cold working on hardness.

TABLE 54.—EFFECT OF COLD WORK ON THE HARDNESS OF STEEL

Material	Hardness	
	Brinell	Scleroscope
Wrought iron, C = 0.11 per cent. Hot rolled.....	118	24
Wrought iron after maximum reduction—48.3 per cent.....	201	46
Electric steel, C = 0.12 per cent. Hot rolled.....	135	26
Electric steel after maximum reduction—70.4 per cent.....	265	57
Electric steel, C = 0.27 per cent. Hot rolled.....	130	22
Electric steel after maximum reduction—74.2 per cent.....	249	58
Electric steel, C = 0.62 per cent. Hot rolled.....	185	33
Electric steel after maximum reduction—44.3 per cent.....	326	59
Electric steel, C = 0.98 per cent. Hot rolled.....	285	59
Electric steel after maximum reduction—32.8 per cent.....	361	52

The results of the scleroscope proved to be rather irregular.

It was difficult to determine the effect of different degrees of cold working on the specific gravity, but it was found that annealing increases the density of hard drawn steel more in the case of mild steel than of high carbon steel. The same was true of electrical resistance. The only conclusion drawn was that cold

TABLE 55.—EFFECT OF COLD WORK ON THE MAGNETIC PROPERTIES OF STEEL

Carbon, per cent.	Treatment	Max. μ	Hat μ max.	Remanence	Coercive force	Hysteresis, erg per cm. ²
0.07	Untreated.....	1,091	5.5	8,200	3.5	24,400
0.07	Drawn: 96.5 per cent. reduction.	380	22.5	9,800	14.8	78,650
0.55	Untreated.....	471	17.0	9,500	10.0	60,100
0.55	Drawn: 86.5 per cent. reduction.	297	31.6	11,600	18.5	104,000
0.78	Untreated.....	327	27.5	10,200	15.0	80,600
0.78	Drawn: 67.5 per cent. reduction.	281	39.3	11,800	22.0	129,500

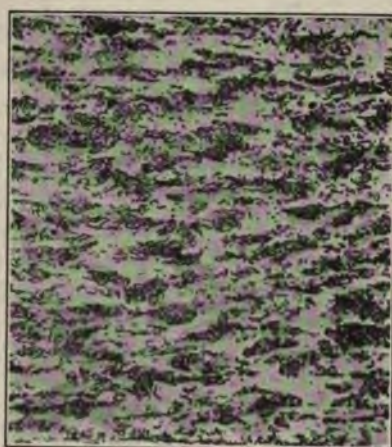
drawing distinctly increases the electrical resistance of pure iron;¹ but it was uncertain that the same was true of medium and high carbon steels. The influence of cold drawing on the magnetic properties is best shown by Table 55.

Charpy has shown (1895) that the first deformations have the greatest effect in increasing the remanent magnetism and that further deformations increase it by such smaller amounts.

The difference in potential between the strained and unstrained material (cold worked specimen: acid N/10 iron sulphate: annealed specimen) is given by Table 56.

TABLE 56.—EFFECT OF COLD WORK ON THE ELECTROLYTIC POTENTIAL OF MILD STEEL

Basic Bessemer	Measured immediately	After 4 hrs.
Mild steel, C = 0.07 per cent.	— 4.1 Mv	—30.0 Mv
After 7 drawings	—13.0 Mv	—22.0 Mv



× 500

FIG. 88.—Carbon 0.56 per cent. Effect of cold working. (Hanemann.)

Microstructure.—Cold working was seen to produce an elongation of the crystals in the direction of the deformation which increased with the amount of reduction. The characteristic structure of cold-worked medium-carbon steel is shown in Fig. 88. Cold working shattered the slag of wrought iron and forced

¹ It is difficult to reconcile this to the statement of CAMPBELL referred to on page 187, and with the same conclusion of VAN DEN BROEK, *Carnegie Sch. Mem.*, Iron and Steel Inst., 1918, Vol. 9, p. 146.

iron into the cracks giving the slag veins a jagged appearance. This structure is characteristic of cold worked wrought iron even after annealing.

Effect of Annealing on Cold-Worked Steel.—The second part of the work was devoted to the changes produced in cold-worked mild steel by annealing. The material used for this study was a low carbon basic Bessemer mild steel wire which had been reduced from 7 mm. to 2.7 mm. diameter in five passes, making the total reduction 85 per cent. Its chemical composition was carbon 0.080, manganese 0.39, silicon 0.008, sulphur 0.056, phosphorus 0.059, expressed in percentages. The effect of annealing at various temperatures up to 1100°C. was determined. It was seen that annealing (even at low temperatures) tends to cause a reversion to the original state. This change does not increase uniformly with increasing temperature but, at least for this steel, is much more pronounced at about 520°C. at which temperature the change to the original soft condition is nearly complete.¹

The influence of annealing on the tensile properties is given in Table 57.

TABLE 57.—EFFECT OF ANNEALING ON COLD-WORKED MILD STEEL

Property	After Drawing	Annealed for 20 minutes at		
		436°	531°	1070°
T.S.	122,800 lbs.	107,000 lbs.	64,000 lbs.	54,000 lbs.
Y.P.			39,000 lbs.	39,000 lbs.
Elong.	5.5 per cent.	9.3 per cent.	21.0 per cent.	29.3 per cent.
R.A.	27.3 per cent.	37.2 per cent.	52.8 per cent.	68.4 per cent.

The "flexibility" was determined by bending tests, taking the

¹ MUIR had reported that the normal condition of wrought iron and steel which had been hardened by overstrain can be restored by annealing at any temperature above 300°C.—*Trans. Roy. Phil. Soc.*, 1902, Vol. 198, p. 1. BAUER, reporting on the effect of annealing steel (C = 0.29 per cent.; Mn = 0.98 per cent.; Si = 0.08 per cent.; P = 0.031 per cent.; S = 0.048 per cent.; Cu = 0.06 per cent.; Cr = 0.015 per cent.) which had been cold worked, found the effect to be noticeable at 400°C. The impact tests showed a drop in resistance up to 300°C. and then a gradual increase up to 900°C.—*Stahl u. Eisen*, 1916, Vol. 36, p. 484. Similar results were obtained by MATSUDA on steel wire containing 0.8 per cent. C and reduced 66 per cent. by cold drawing—*Sci. Rep. Tohoku Imp. Univ.*, 1916, Vol. 5, p. 121.

number of bends which the wire could sustain before fracturing as a measure of the toughness. The results were as follows:

Annealing temperature deg. C.	0	500	520	1000
Number of bends.	11	16	27	31

For the influence of cold working and annealing on the magnetic properties, reference should be made to the original paper as the results are both lengthy and important. As an example, it was found that the curve for remanent magnetism rises from 9,450 in hard drawn material to 15,050 for an annealing temperature of 531°, and that it drops off to 10,050 for an annealing temperature of 1072°. To remove the difference in potential between the strained and annealed material, it was sufficient to anneal at 600° to 625°C.

An interesting case of excessive grain growth in low-carbon steel on annealing after mechanical deformation, was reported by Charpy,¹ who annealed a piece of soft steel containing a Brinell indentation and found a well-defined zone of abnormally large grains a short distance away from the impression. The essential points seemed to be severe plastic deformation, an anneal at about 700°C. for at least six hours, and that the material must be low in carbon. Charpy's phenomenon was further reported on by Le Chatelier.² Investigation along this line has since been continued by Sauveur,³ and Chappell,⁴ and the practical import of this remarkable effect has been dealt with by Sherry.⁵ Sauveur pointed out in particular that excessive grain growth depended on a critical strain while a detailed investigation of grain growth phenomena and "equiaxing" temperatures has been made by Jeffries.⁶ This question is important in work's practice

¹ *Rev. de Met.*, 1910, Vol. 7, p. 655.

² *Rev. de Met.*, 1911, Vol. 8, p. 370.

³ *Proc. Int. Assoc. Test. Mat.*, New York, 1912.

⁴ *Journ. Iron and Steel Inst.*, 1914, Vol. 89, No. 1, p. 460.

⁵ *Met. and Chem. Eng.*, 1912, Vol. 10, p. 666; also *Iron Age*, 1916, Vol. 98, p. 76.

⁶ While it is not intended to deal at length with the phenomena of grain growth on annealing, at this time, the work of Dr. Jeffries is deemed to be of sufficient value and importance to warrant a bibliography here for general reference. Other important papers are also listed which deal with the same phenomena. JEFFRIES, "Grain Growth Phenomena in Metals," *Trans. Amer. Inst. Min. Eng.*, Vol. 54, (1916), p. 571; see also discussion of paper by MATHEWSON and PHILLIPS, p. 658; "Grain Size Determination in Metals and the Importance of Such Information," *Trans. Faraday Soc.*, 1916; "Grain

and will be dealt with at length under "Heat Treatment" in Part III.

Microstructure.—The characteristic fibrous structure of the cold-worked steel used by Goerens was replaced by granular structure (equiaxial) at 520°. This temperature is the same as that corresponding to the change in properties. Other materials might require temperatures up to 600°C.

We have already seen that lamellar pearlite is converted into granular pearlite when it is annealed at about 700°C. This effect is accelerated if the steel has been previously cold-worked and the action begins at about 500°C. At 700°C., the "divorce" is complete in from two to four hours (for thin and thick lamellar pearlite resp.) whereas non-deformed lamellar pearlite would require several days annealing (Whiteley). Fig. 89 taken from the work of Hanemann and Lind¹ illustrates this effect.²

Cast Steel.—The structure of an ordinary steel casting without any treatment is shown in Fig. 90. This structure is recognized at once as Widmanstätten structure and is due to (a) the formation of comparatively large austenite crystals, and (b) to the fairly rapid but not greatly accelerated rate of cooling through the transformation range. Under these circumstances the typical ferrite precipitation results. Steel in this condition corresponds

Size Inheritance in Iron and Steel," *Trans. Amer. Inst. Min. Eng.*, 1917; "The Amorphous Metal Hypothesis and Equicohesive Temperatures," *Trans. Amer. Inst. Met.*, 1917, Vol. 11, p. 300; "Grain Size Measurements," *Met. and Chem. Eng.*, 1918; "Grain Growth in Metals," *Journ. Inst. Met.*, 1918, No. 2, p. 109; "Metallography of Tungsten," *Trans. Amer. Inst. Min. Eng.*, 1918; "Effect of Temperature, Deformation and Grain Size on the Mechanical Properties of Metals," *Trans. Amer. Inst. Min. Eng.*, 1919; STEAD, "Crystalline Structure of Iron and Steel," *Journ. Iron and Steel Inst.*, 1898, No. 1, p. 145; "Brittleness Produced in Soft Steel by Annealing," *Ibid.*, 1898, No. 2, p. 137; JOISTEN, "Einfluss der thermischen Behandlung auf die Korngrösse des Eisens," *Metallurgie*, 1910, Vol. 7, p. 456; ROBIN, "Recherches sur le Developpement des Métaux par Recuit après Ecrouissage," *Rev. de Metallurgie*, 1913, Vol. 10, p. 722, see also p. 758; RUDER, "Grain Growth in Silicon Steel," *Trans. Amer. Inst. Min. Eng.*, 1913, Vol. 47, p. 569; CHAPPELL, "Recrystallization of Deformed Iron," *Journ. Iron and Steel Inst.*, 1914, No. 1, p. 460; HOWE, See *Trans. Amer. Inst. Min. Eng.* Vol. 56, p. 551.

¹ *Stahl u. Eisen*, 1913, Vol. 33, p. 551.

² WHITELEY has shown recently that this divorcing raises the values for combined carbon as determined by the EGGERTZ test. *Journ. Iron and Steel Inst.*, 1918, No. 1, p. 333.

to over-heated steel, and consequently does not possess its best properties. Like over-heated steel, it can be improved by heat treatment. This fact is being grasped by steel makers and at present steel castings are being given more attention than they were formerly. Goerens and Meyer¹ have shown that complete "grain refinement" is brought about by reheating to above A_{c_3} for at least 15 minutes (the time varying with the thickness of the casting) followed by slow cooling at least to black heat. The structure produced by this operation is also shown in Fig. 90.

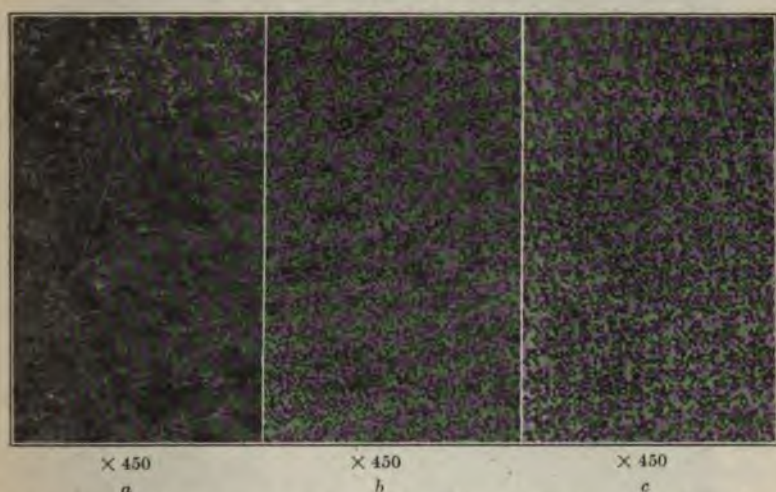


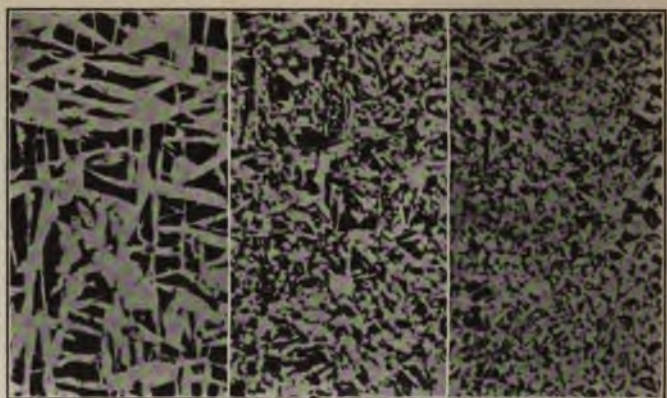
FIG. 89.—Effect of cold rolling and annealing on the structure of pearlite. (a) annealed; (b) cold rolled and annealed; (c) cold rolled and annealed several times. (Hanemann.)

Steel castings can be further improved in their properties by cooling in air from above A_{c_3} , or even quenching in water. In the latter case the castings are tempered, which operation also removes the strains set up during quenching. The benefits derived from this treatment have been pointed out by Hall² who shows that by using low carbon (0.25 per cent.) and high manganese (1.25 per cent.), castings with equally as good static properties and resistance to alternating stresses and far greater toughness can be secured than by using higher carbon steel (0.45 per cent.).

The general improvement in the properties of steel castings

¹ *Metallurgie*, 1911, vol. 8.

² The Steel Foundry.



1

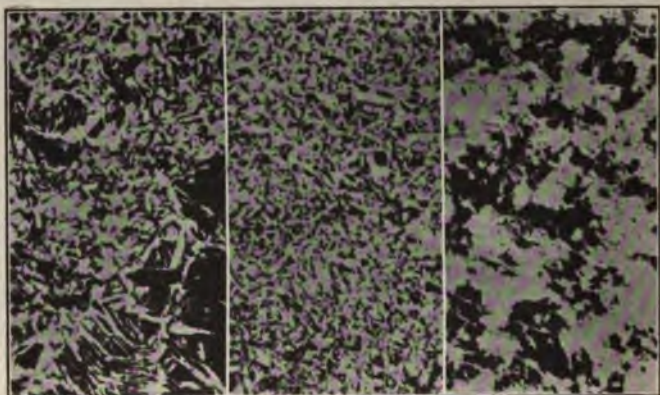
As cast.

2

Annealed 1550°F., air cooled.

3

Annealed 1650°F., air cooled



4

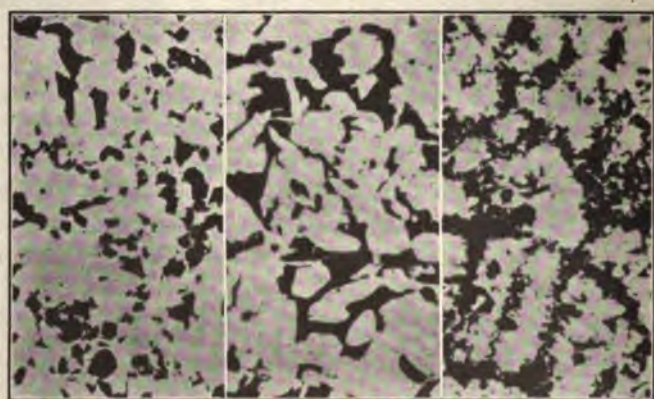
Annealed 1750°F., air cooled.

5

Same as 2, repeated twice.

6

Annealed 1550°F., furnace cooled.



7

Annealed 1650°F., furnace cooled.

8

Annealed 1750°F., furnace cooled.

9

Same as 6, repeated twice.

FIG. 90.—Basic OH steel casting, C 0.26; Mn 0.66; Si 0.34. ($\times 100$)
 The specimens were held 20 min. at temperature. (The American Steel Foundries. By permission of Prof. Fulton.)

by heat treatment has been shown by Hall and by Young, Pease and Strand.¹ The general conclusion of the latter was that "the heat treatment increases the elastic limit about 50 per cent., without any material change in elongation."² This can be shown as follows:

TABLE 58.—HEAT-TREATED VS. ANNEALED STEEL CASTINGS

	0.20 per cent. C		0.55 per cent. C	
	Annealed	Heat treated	Annealed	Heat treated
Elastic limit, lbs. per sq. in.	30,000	45,000	43,000	65,000
Tensile strength, lbs. per sq. in. .	60,000	74,000	92,500	114,000
Elongation, per cent.	13.5	13.5	10.2	9.9

It was pointed out at the time that, according to shock tests, a treatment of at least several hours at 600° is required to remove the internal strains due to quenching a casting in water, but that it is perfectly possible to do so in this manner.

The importance of annealing steel castings has also been very clearly shown by Oberhoffer in a series of papers dealing with the properties of annealed and unannealed castings. The attention of American metallurgists has been drawn to this important subject by Cone, whose results along with certain other results, are given in the following table.

¹ HALL, "Shock Tests of Cast Steels," *Trans. Amer. Inst. Mining Eng.*, 1914, Vol. 47, and discussion by HOWE in particular; YOUNG, PEASE and STRAND, "The Heat Treatment of Steel Castings," *Trans. Amer. Inst. Mining Eng.*, 1914, Vol. 50, p. 424.

² The importance of heat treating steel castings has been dealt with in considerable detail by HALL, NISSEN and TAYLOR, *Bull. Amer. Inst. Min. Met. Eng.*, 1919, No. 153, p. 2881.

TABLE 59.—PROPERTIES OF STEEL CASTINGS

Composition	Treatment	Y. P.	T. S.	Elong.	R. A.	Tough. mkg.
C = 0.11; Mn = 0.88 (Ob)	As cast.....	26,000	58,500	25.9b	30.0	3.64 Ch.
C = 0.11; Mn = 0.88 (Ob)	Annealed, 920°	37,000	60,000	29.9b	59.2	17.16 Ch.
C = 0.27; Mn = 0.60 (Ob)	As cast.....	32,700	67,000	14.6b	17.0	
C = 0.27; Mn = 0.60 (Ob)	Annealed, 850°	39,800	73,000	22.5b	29.7	
C = 0.23; Mn = 0.98 (Ob)	As cast.....	30,000	63,800	14.8b	26.9	1.94 Ch.
C = 0.23; Mn = 0.98 (Ob)	Annealed, 850°	40,600	68,000	29.0b	51.7	7.22 Ch.
C = 0.66; Mn = 0.92 (Ob)	As cast.....	41,700	82,500	3.37b	3.8	1.36 Ch.
C = 0.66; Mn = 0.92 (Ob)	Annealed, 790°	46,600	84,000	7.6b	12.8	1.42 Ch.
C = 0.37; Mn = 0.62 (C)	As cast.....	38,000	78,000	24.0a	27.5	
C = 0.37; Mn = 0.62 (C)	Annealed.....	41,400	80,400	24.0a	37.0	
C = 0.37; Mn = 0.62 (C)	Air cooled.....	48,000	85,500	25.0a	37.2	
Electric steel:						
C = 0.23; Mn = 0.50 (C)	As cast.....	33,700	64,800	25.0a	34.2	
C = 0.23; Mn = 0.50 (C)	Annealed.....	52,000	71,400	25.0a	40.8	
Electric steel:						
C = 0.29; Mn = 0.59 (C)	As cast.....	42,500	72,500	26.0a	29.0	
C = 0.29; Mn = 0.59 (C)	Annealed.....	59,700	80,900	19.5a	20.2	
Electric steel:						
C = 0.46 (C)	As cast.....	66,480	102,740	3.0a	4.9	
C = 0.46 (C)	Air cooled from Acs	72,860	104,270	18.0a	27.1	

(Ob) = Oberhffer: *Stahl u. Eisen*, 1912, No. 1, p. 889; 1913, No. 1, p. 891.(C) = Cone: *Iron Age*.

Elongation, a = on two inches; b = on (l = 10d).

Ch. = Charpy Test.

Composition	Treatment and remarks	Y. P.	T. S.	Elong.	R. A.	Tough. mkg
C = 0.10 Mn = 0.23 Ha.	As cast. Bend test 50°..... 900°—3 hrs. Cool 40 min. Bend test 180°.....	23,900 28,750	50,000 55,400	35.2a 38.5a	47.8 67.0	2.5 Frem. 20.0 Frem.
C = 0.21 Mn = 1.17 Ha.	900°—aqua, 650° reheat. Bend test 180°.....	71,650	91,900	20.4a	50.2	21.0 Frem.
C = 0.42 Mn = 0.73 Ha.	900°—air cooled; reheat 700° furnace cooled. 10,709,600 rev. at 28270# and 296,400 rev. at 38870# C.	46,000	82,100	8.4a	9.8	7.5 Frem.
C = 0.44 Mn = 0.59 Ha.	900°—air cooled, reheat 690° furnace cooled..... 5,697,000 rev. at 28270# Broke. C.	43,000	76,200	14.64a	15.11	5.0 Frem.
C = 0.23 Mn = 1.07 Ha.	900°—aqua, reheat 680°, air cooled..... 10,475,000 rev. at 28270# and 619,700 rev. at 38870#	44,400	67,200	14.19a	31.3	32.0 Frem.
C = 0.18 Mn = 0.09 A.	As cast. Low Mn..... Annealed. Low Mn.....	26,600 21,000	45,000 53,600	19.5b 31.0b	29.1 47.0	
C = 0.37 Mn = 0.08 A.	As cast. Low Mn..... Annealed. Low Mn.....	33,000 23,000	48,800 46,600	5.0b 12.5b	5.9 19.8	
C = 0.50 Mn = 0.07 A.	As cast. Low Mn..... Annealed. Low Mn.....	39,200 23,600	44,500 55,000	2.5b 16.0b	1.7 18.4	
C = 0.70 Mn = 0.03 A.	As cast. Low Mn..... Annealed. Low Mn.....	49,800 41,500	72,500 63,500	2.0b 4.0b	1.8 1.7	

Ha. = Hall: The Steel Foundry.

C = White-Souther endurance testing machine.

A. = Arnold: *Journ. Iron & Steel Inst.*, 1901, No. 1, p. 178.

Elongation, a = on 2 in.; b = on (l = 10d).

PROPERTIES OF STEEL CASTINGS

Material	Composition			Yield point	Tensile strength, lb. per sq. in.	Elongation, per cent.	R. A., per cent.
	C	Mn	Si				
1. Dynamo and motor castings.	0.10-0.15	0.20-0.30	0.20-0.40	53,000-62,500	20-30	90
2. Ship and machine castings. Locomotive castings.	0.25-0.30	0.30-0.50	0.30	53,000-62,500	20	55
					57,000-71,000	18	
					64,000-78,000	12	
3. Hard, resistant castings	0.50-0.70	0.60-0.80	0.35	40,000	71,000-100,000		
4. Castings for crusher parts. Hard and tough. Must be ground	50,000	85,000-100,000	2-6	
5. Railway castings	0.25-0.30	$\frac{1}{2}$ of T. S.	60,000	25	40
6. Industrial and marine castings	0.25-0.30	$\frac{1}{2}$ of T. S.	65,000	22	40
7. Same as 6. Higher carbon	$\frac{1}{3}$ of T. S.	80,000	17	25

1-4. Geiger. Handbuch d. Eisen u. Stahlgießerei. Vol. I.

5-7. Cone. Iron Age, 1913, Vol. 92, No. 2, p. 223.

The Effect of Temperature on the Properties of Steel.—It has been abundantly shown that the tensile strength of steel is greater at some temperature between 200 and 350°C. than at room temperature, the position of the maximum varying with the carbon content. Before attaining this maximum, however, the tensile strength may pass through a shallow minimum somewhere between 60 and 200°C. (Rheinhold). The reduction of area varies inversely as the tensile strength and at 600°C. may be as high as 90 per cent. The elongation also varies inversely as the tensile strength. It has already been stated that the yield point drops with rise in temperature so that at no other temperature can we get as good a combination of properties as at room temperature.¹ Just recently the Bureau of Standards has conducted two series of tests on boiler plate in which measurements of the proportional limit were made. It was found that the proportional limit of the fire box grade rose from 23,300 lbs. at room temperature to 26,600 lbs. at 156°C. and remained around 25,000 lbs. even up to 243°, above which temperature it fell to 11,400 lbs. at 466°. The tensile strength rose from 59,000 lbs. at room temperature to 66,700 lbs. at 295° and then fell to 42,000 lbs. at 466°. The elongation fell from 37.75 per cent. at room temperature to 19.8 per cent. at 243 deg. and then rose to 39.2 per cent. at 466° while the reduction of area fell from 57.1 per cent. to 45.1 per cent. at 243° and then rose to 67.7 per cent. at 466°. The marine boiler plate grade varied in just about the same manner although the proportional limit failed to show the maximum. The proportional limit and tensile strength were found to be as follows: at room temperature, 31,200 lbs. and 66,700 lbs.; at 293°C., 22,450 and 72,500 lbs. and at 465° C. 12,500 and 55,600 lbs.² Rudeloff, on the other hand found no increase in the proportional limit above room temperature while Warziniok reports a fall in the yield point.³ This agrees with

¹ See Part I, p. 239. RHEINHOLD, *Ferrum*, 1916, Vol. 13, p. 97.

² FRENCH, Amer. Inst. Min. Met. Eng., *Mining and Metallurgy*, Feb., 1920, No. 158, Sect. 15. The firebox grade contained 0.19% C and 0.43% Mn while the marine boiler grade contained 0.25% C and 0.38% Mn. Dr. Jeffries sees in these results the manifestation of low temperature allotropy in iron, but it is well to bear in mind for the present that the data are insufficient for such an assumption and also that criteria for allotropy over this range have not been shown by the more accurate and trustworthy physical data.

³ RUDELLOFF, Int. Soc. Test. Mat., 1909, Sec. VI., Paper 11.

the results obtained at the Watertown Arsenal as given in the Tests of Metals of 1888. The importance of the physical and mechanical properties at elevated temperatures is certainly great enough to warrant more work in this field with a view of determining, for example, the effects of composition, rate of loading, structure, atmosphere, etc., on the properties.

It is important to note here that the toughness of steel, as determined by the Charpy test, has high values only at room temperature and at 600°C. At low temperatures and at temperatures in the neighborhood of 420°C. (the minimum) the impact figures are low. While the data for settling such a point are insufficient at the present writing, it does not seem that the maxima of the tensile strength coincide with the minimum of the impact figures obtained with notched bars.¹ The phenomenon known as "blue brittleness" generally refers to deficiency in ductility, as shown by abnormally low elongations and reductions of area in the tensile test, rather than to deficiency in toughness as shown by impact tests. This blue brittleness occurs at temperatures corresponding to blue temper colors and is so pronounced that it is dangerous to work steel over this temperature range.²

The Magnetic Properties of Steel.—Considerable steel is used at present in the form of steel castings and as sheets in the construction of transformers, electro-magnets, and electrical machinery. The material used has more of the properties of pure iron than of steel and has already been described. Another important technical use of steel is in the construction of permanent magnets such as are used in magnetos. We shall consider here the effect of composition, temperature, etc., on the magnetic properties of iron and steel, and another important, though frequently neglected, factor—the physical condition of the material as affected by both heat and mechanical treatment. This latter phase of the subject is now receiving more attention with the development of the work on the correlation of the magnetic characteristics and the mechanical properties. In the literature many constants on many different materials have been given with insufficient information on the condition of the material

¹ GOERENS and HARTEL, *Zeit. anorg. Chem.*, 1913, Vol. 81, p. 130.

² DR. JEFFRIES has discussed the phenomena of blue brittleness in considerable detail and has outlined work the results of which should throw light on this important subject and serve to clear up the discrepancies which are so glaring at present. *Mining and Metallurgy*, Amer. Inst. Min. Met. Eng., Feb., 1920.

tested and it is to be hoped that steps will be taken in the future by physicists more clearly to define the specimens examined.

The Effect of Chemical Composition.—Tables 60 and 61,¹ taken from the Smithsonian Tables, give magnetic constants for various materials.

In the early work of Barret, Brown and Hadfield,² the tremendous influence of composition on the magnetic properties was shown; thus alloys containing more than 70 per cent. iron were found which were quite non-magnetic while an aluminum and a silicon alloy were found which, in low field strengths, were more magnetic than iron. The alloy with 2.25 per cent. aluminum has twice the permeability of iron in small fields while the alloy with 2.50 per cent. silicon, now known as silicon steel, while less permeable than the aluminum alloy was more so than iron in small fields. In particular, the effect of elements such as carbon, manganese, nickel, tungsten, aluminum, silicon, chromium and copper, on the electrical and magnetic properties of iron was studied. Among the many practical aspects of the paper were its bearing on the aging of iron and the hysteresis loss.

It has not been possible, so far, to establish a definite relationship between the magnetic properties of the iron alloys and the element added. This has led Ruder to draw the somewhat unusual conclusion, after studying the effect of adding carbon, silicon, aluminum arsenic, tin, cobalt, copper, chromium, tungsten, molybdenum, etc., to iron, that magnetism is not an atomic property but that it is a property of the crystalline structure of the material and must be attacked by some such method as the X-ray method of Bragg.³ Gumlich⁴ points out, in this connection, that the influence of the element depends upon the heat treatment and gives, as an example, carbon which, when dissolved, exerts

¹ These results are for the highest magnetizing force used—240. To obtain the maximum magnetization, subtract the magnetizing force (240) from the maximum induction and then divide by 4π . The "demagnetizing force" is the magnetizing force which had to be applied in order to have no residual magnetization after previous magnetization in the opposite direction to the "maximum induction" stated in the table. The energy dissipated (approx.) = coercive force \times maximum induction divided by π . In nos. 32 and 33, C = graphitic carbon.

² *Journ. Inst. Electrical Eng.*, 1902, Vol. 31, p. 674.

³ *General Electric Review*, Vol. 18, p. 197.

⁴ *Trans. Faraday Society*, April 23, 1912. See also *Met. and Chem. Engin.*, 1912, Vol. 10, p. 402.

TABLE 60.—MAGNETIC PROPERTIES OF IRON AND STEEL

	Electrolytic Fe	Good cast steel	Poor cast steel	Steel	Cast iron	Electrical sheets	
						Ordinary	Silicon steel
Chemical composition in per cent. <div> <div>C.</div> <div>Si.</div> <div>Mn.</div> <div>P.</div> <div>S.</div> </div>	0.024	0.044	0.56	0.99	3.11	0.036	0.036
	0.004	0.004	0.18	0.10	3.27	0.330	3.90
	0.008	0.40	0.29	0.40	0.56	0.260	0.090
	0.008	0.044	0.076	0.04	1.05	0.040	0.009
	0.001	0.027	0.035	0.07	0.06	0.068	0.006
Coercive force.....	2.83 (0.36)	1.51 (0.37)	7.1 (44.3)	16.7 (52.4)	11.4 (4.6)	((1.30))	((0.77))
Residual B.....	11,400 (10,800)	10,600 (11,000)	10,500 (10,500)	13,000 (7,500)	5,100 (5,350)	((9,400))	((9,850))
Maximum permeability.....	1,850 (14,400)	3,550 (14,800)	700 (170)	375 (110)	240 (600)	((3,270))	((9,130))
B for H = 150.....	19,200 (18,900)	18,800 (19,100)	17,400 (15,400)	16,700 (11,700)	10,400 (11,000)	((18,200))	((17,550))
4 I for saturation.....	21,620 (21,630)	21,420 (21,420)	20,600 (20,200)	19,800 (18,000)	16,400 (16,800)	((20,500))	((19,260))

E. Gumlich, *Zeit. f. Electrochemie*, 15, p. 599; 1909.

Double brackets indicate annealing at 800°C. in vacuum.

Single brackets indicate hardening by quenching from cherry red.

No.	Description	Temper	Chemical Analysis					Specific elec. resistance	Magnetic properties			
			Total C	Mn	S	Si	P		Max. induction	Resid. induction	Coercive force	Demagnetizing force per cycle
1	Wrought iron.....	Annealed	0.01378	18,251	7,248	2.30
2	Malleable cast Fe.....	Annealed	0.03254	12,408	7,479	8.80	13,356
3	Gray cast Fe.....	0.03254	12,408	7,479	8.80	34,742
4	Best iron steel.....	0.01050	10,783	3,928	3.80	13,037
5	Whitworth mild steel.....	Annealed	0.045	0.300	0.030	None	0.040	0.01050	10,783	3,928	3.80	17,137
6	Whitworth mild steel.....	Annealed	0.090	0.153	0.016	None	0.042	0.01080	18,196	7,860	2.96	10,289
7	Whitworth mild steel.....	Oil-hardened	0.320	0.438	0.017	0.0420	0.035	0.01446	19,840	7,080	6.73	40,120
8	Whitworth mild steel.....	Annealed	0.800	0.165	0.005	0.081	0.019	0.01390	18,796	11,040	11.00	65,786
9	Whitworth mild steel.....	Oil-hardened	0.800	0.165	0.005	0.081	0.019	0.01559	16,190	10,740	8.26	42,366
10	Hadfield's Mn steel.....	1.805	12.36	0.038	0.204	0.070	0.01695	16,190	8,736	19.38	99,401
11	Manganese steel.....	As forged	0.074	4.730	0.023	0.608	0.078	0.05554	4,310	2,202	23.50	34,567
12	Manganese steel.....	Annealed	0.074	4.730	0.023	0.608	0.078	0.03298	10,578	5,848	33.86	113,963
13	Manganese steel.....	Oil-hardened	0.074	4.730	0.023	0.608	0.078	0.03298	10,578	5,848	33.86	113,963
14	Manganese steel.....	As forged	1.298	8.740	0.024	0.094	0.075	0.03556	4,769	2,158	27.64	41,941
15	Manganese steel.....	Annealed	1.298	8.740	0.024	0.094	0.075	0.03556	4,769	2,158	27.64	41,941
16	Manganese steel.....	Oil-hardened	1.298	8.740	0.024	0.094	0.075	0.03556	4,769	2,158	27.64	41,941
17	Manganese steel.....	As forged	0.685	0.694	0.024	0.094	0.075	0.03556	4,769	2,158	27.64	41,941
18	Silicon steel.....	Annealed	0.685	0.694	0.024	0.094	0.075	0.03556	4,769	2,158	27.64	41,941
19	Silicon steel.....	Oil-hardened	0.685	0.694	0.024	0.094	0.075	0.03556	4,769	2,158	27.64	41,941
20	Chrome steel.....	As forged	0.532	0.393	0.020	0.220	0.041	0.07066	1,955	540	24.50	15,474
21	Chrome steel.....	Annealed	0.532	0.393	0.020	0.220	0.041	0.07066	1,955	540	24.50	15,474
22	Chrome steel.....	Oil-hardened	0.532	0.393	0.020	0.220	0.041	0.07066	1,955	540	24.50	15,474
23	Chrome steel.....	As forged	0.887	0.028	0.020	0.134	0.043	0.01791	13,293	6,480	18.40	85,944
24	Chrome steel.....	Annealed	0.887	0.028	0.020	0.134	0.043	0.01791	13,293	6,480	18.40	85,944
25	Chrome steel.....	Oil-hardened	0.887	0.028	0.020	0.134	0.043	0.01791	13,293	6,480	18.40	85,944
26	Tungsten steel.....	As forged	1.357	0.036	None	0.043	0.047	0.02249	16,498	11,008	15.30	16.93
27	Tungsten steel.....	Annealed	1.357	0.036	None	0.043	0.047	0.02249	16,498	11,008	15.30	16.93
28	Tungsten steel.....	Hardened in cold water	1.357	0.036	None	0.043	0.047	0.02274	15,610	9,482	30.10	34.70
29	Tungsten steel.....	Hardened in tepid water	1.357	0.036	None	0.043	0.047	0.02249	15,610	9,482	30.10	34.70
30	Tungsten steel (Fr).....	Oil-hardened	0.511	0.825	None	0.021	0.028	0.03604	14,480	8,643	47.07	64.46
31	Tungsten steel.....	Very hard	0.511	0.825	None	0.021	0.028	0.03604	14,480	8,643	47.07	64.46
32	Gray cast iron.....	3.455	0.173	0.042	2.044	0.131	0.04427	12,153	9,818	21.20	70.69
33	Mottled cast Fe.....	2.851	0.610	0.105	1.476	0.435	0.01400	10,546	5,108	13.97	17.03
34	White cast iron.....	2.036	0.386	0.467	0.764	0.438	0.06286	10,546	5,108	13.97	17.03
35	Spiegeleisen.....	4.510	7.970	Trace	0.502	0.128	0.05061	9,342	5,564	12.24	20.40
								0.10520	385	77		36,383

its strongest influence by increasing the coercive force and remanent magnetism and lessening the permeability.

These two conclusions are also verified by the work of Hadfield and Hopkinson¹ although these authors do point out that the effect of carbon, at least in annealed "straight-carbon" steels, can be predicted from the amount of carbon present. They found that the specific magnetism is lowered by a percentage equal to six times the per cent of carbon present. In general, as the carbon content increases, the intensity of magnetization and the permeability decrease, and the remanent magnetism and coercive force increase.² Accordingly transformer sheets should contain a small amount of carbon preferably below 0.10 per cent.

The effect of silicon is to decrease the hysteresis loss and, by increasing the electrical resistance, to reduce the eddy current losses. Its influence on the permeability depends upon the field strength:—in weak fields silicon increases the permeability, but in fields of over 10 gauss it lowers the permeability. Ordinarily "silicon steel" for transformers contains only small percentages of carbon, but if carbon is present, the silicon renders the carbon less effective in lowering the magnetism.³ Silicon steel is therefore very valuable for use in electrical machinery and its properties will be considered in the next chapter.

The influence of manganese, sulphur, and phosphorus, in small amounts is not well known but in transformer sheets it is generally held desirable to keep the manganese under 0.3 per cent. and the sulphur and phosphorus as low as possible, preferably under 0.035 per cent. Titanium, in small amounts, is said to improve the permeability and lower the hysteresis of pure iron, but this can be accomplished only with the pure titanium.⁴

The Effect of Temperature.—The loss of magnetism, as measured by the ability of iron to attract a magnetic needle when heated, has long been used to indicate the A_2 or magnetic transformation in iron and the low-carbon steels. This work in recent years has been considerably amplified and extended to the study of the magnetic properties and the constitution of

¹ *Journ. Inst. Elec. Eng.*, 1911, Vol. 46, p. 235.

² See NOLLY and VEYRET, *Proc. Sixth Cong. Int. Assoc. Test. Mater.*, New York, 1912, IX, 5.

³ HADFIELD and HOPKINSON, *Loc. cit.*

⁴ APPLGATE, *Rev. Poly. Inst. N. Y., Eng. and Sci. Series No. 5.*

steel.¹ Larroque, as early as 1889, showed that the low and medium-carbon steels show two critical points, the higher one (A_1) being less important than the lower (A_2), while the high carbon steels show only one critical point (A_1).² It is now known that steels containing up to ca. 0.43 per cent. carbon show a constant magnetic transformation point at $Ac_2 = Ar_2$; that above this temperature they are weakly magnetic but that at Ac_2 the magnetism practically disappears and that in the higher carbon steels the magnetic transformation point is subject to

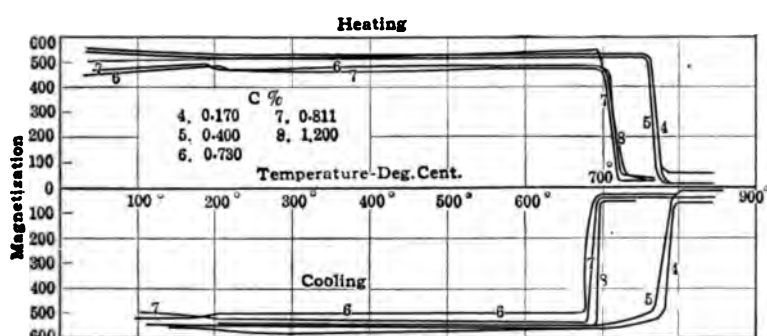


FIG. 91.—Magnetic transformations in steel. (6th Congress. Int. Soc. Test. Mat.)

hysteresis. These points can be illustrated by the curves in Fig. 91 and Fig. 92 taken from the work of the chemical laboratories of Schneider & Company showing the intensity of magnetization of a series of carbon steels. Recently it has been stated by Honda³ that the loss of magnetism on heating occurs at 790°C. irrespective of the carbon content. The curves given of magnetization vs. temperature and simultaneous heating and cooling curves do not corroborate this temperature, principally because the temperatures of the heat effects (eutectoid transformation) are placed about 30 to 40°C. too high. Correcting for this would bring the loss of magnetism down to about 750°C. which is still above the eutectoid point, as is evident from the

¹ See SMITH and GUILD, *Trans. Roy. Soc., London*, 215, p. 177. Also *Proc. Physical Soc., London*, 24, 62, p. 342. HONDA and TAKAGI, *Journ. Chemical Soc.*, 1913, Vol. 2, p. 222. The Chemical Laboratories of SCHNEIDER and Company. *Proceed. 6th Cong. Int. Assoc. Test. Mat.*, New York, 1912, II, 4. RUMELIN and MAIRE, *Ferrum*, 1915, Vol. 12, p. 141.

² *La Lumiere Elect.*, 1889, Vol. 30, p. 369.

³ *Journ. Iron and Steel Inst.*, 1915, No. 1, p. 199.

curves. Rumelin and Maire have also located the magnetic transformation point in high carbon steels on heating at 750°C. The work of Smith and Guild, on the other hand, indicates that the magnetic transformation and the A_1 inversion occur simultaneously. The A_1 transformation is placed at 1390°C., which may be said to check the results of thermal analysis.¹

By reference to Figs. 91 and 92 it will be noted that a transformation occurs at about 200°C. This is due to a magnetic transformation of cementite, and has been studied by various

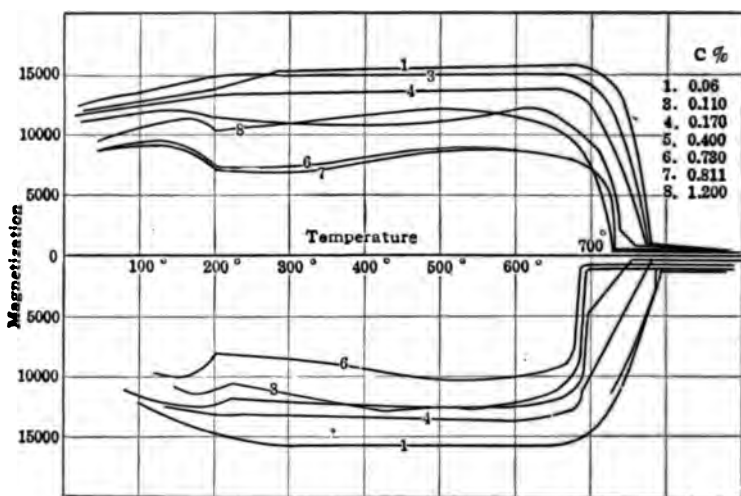


FIG. 92.—Magnetic transformations of steel. (6th Congress. Int. Soc. Test. Mat.)

experimenters.² This transformation is not found in pure iron and increases in intensity with the carbon content. It seems possible to determine the percentage of carbon present by a method based on this effect (Smith).

The magnetic properties of steel have been studied at the temperatures of liquid air but have not as yet produced any very important results.³

¹ ISHIWARA, *Proc. Tokio Math. Phys. Soc.*, 1917 (2) 9, p. 107.

² See ROBIN, *Loc. cit.* HONDA and TAKAGI, *Loc. cit.* MARGARET B. MOIR, *Proc. Roy. Soc. Edinburgh*, 31, p. 505. S. W. J. SMITH, *Proc. Phys. Soc. London*, Vol. 25, p. 77. WILLIAMS, *Phys. Rev.*, Vol. 3, p. 115.

³ See WAGGONER, *Phys. Review*, Vol. 28, p. 393. GRAY and ROSS, *Trans. Faraday Soc.*, 1912, Vol. 8, p. 115.

The temperature coefficient of magnetic permeability is generally very small but it has been pointed out that neglect of this factor may lead to error, due principally to the effect of composition and heat treatment.¹

The effect of temperature on the residual magnetism has been determined for a number of different steels.² Steel rods containing from 0.36 to 1.53 per cent. carbon when magnetized to saturation show a positive residual magnetism. As the temperature is raised the residual magnetism falls to zero at 180 to 200°C. and reaches a maximum negative value at 220°C. becoming zero again at 700 to 850°C. The amount of negative magnetism is greatest for the eutectoid composition. If the reheating does not remove all the residual magnetism, then, on cooling, the negative magnetism increases in amount to about 245°C., falls to zero at 210°C. and attains a fairly large positive value at room temperature. This behavior of steel can be used in a measure to indicate the nature and heat treatment of the steel under consideration.

Heat Treatment and Magnetic Properties.—The heat treatment of magnet steels, required to produce a high coercive force and a high remanence, will be considered under "Magnet Steels" in Part III.

The general effect on the permanent magnetism produced by quenching high carbon steels is well known. This can be seen in Table 62 in which the Brinell hardness number is added to indicate the parallelism between mechanical hardness and permanent magnetism. It should be remarked that this parallelism holds only under certain circumstances and it is known that of two steels differing in hardness, the softer one (quenching in oil as compared to water) can be magnetically more permanent. The effect of reheating quenched steel is to increase the maximum induction and residual induction and to lower the coercive force. This effect is more pronounced on oil-hardened steel than on water hardened steel. In one case, drawing at 315°C. lowered the Brinell hardness of water-quenched steel by 101 points, and of the oil-quenched steel by only 36 points; but the change in B, Br and Hc was greater for the latter bars than for the former,

¹ See SANFORD, *Journ. Frank. Inst.*, 1915, Vol. 179, p. 96.

² See SMITH and GUILD, *Proc. Phys. Soc.*, 1912, Vol. 24, p. 342. ROBIN, *Bull. Soc. Engin. Civil. Series 7*, p. 778. *Mem. Soc. Ing. Civ. de France*, 1912, Vol. 65, p. 778.

so much so that the greater permanence of the oil-quenched bars was practically eliminated. (Matthews.)

TABLE 62.—PROPERTIES OF QUENCHED MAGNET STEEL

No.	Scleroscope hardness	Brinell hardness	B	Br	Hc	Br/Hc
1	73.5	594	16,700	11,415	44.66	256.0
2	63.0	534	14,330	9,040	52.40	172.5
3	70.0	548	15,500	10,285	50.00	205.7

Heat treatment (1) Quenched from 815°C. in cold water—6 bars.

(2) Quenched from 843°C. in oil—6 bars.

(3) Quenched from 843°C. in boiling water—2 bars.

Composition: C = 0.50 per cent.; Si = 0.51 per cent.; Mn = 0.79 per cent. Cr = 0.73 per cent. Reference: Kelly, *G. E. Review*, 1917, Vol. 20, p. 569, on permanent magnets.

The effect of quenching on mild steel, such as is used in electrical machinery, is quite small, as has been shown by Gumlich. This

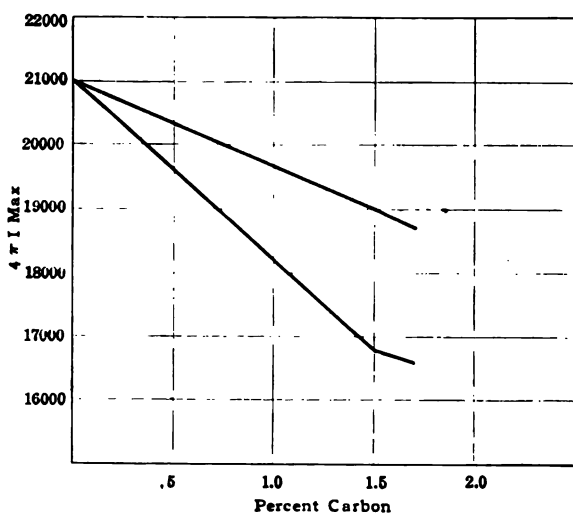


FIG. 93.—Effect of carbon and heat treatment on the magnetic saturation of steel. (Matthews.)

Upper line, after annealing at 930°C. Lower line, after quenching from 850°C.

can also be seen by reference to Fig. 93. This figure also shows that as the carbon content increases the effect of hardening becomes much more pronounced.

Work on heat treatment has brought out the important point

that the magnetic properties of steel depend very greatly upon the microstructure, grain size of the pearlite, etc., and that therefore, it is quite insufficient to use the terms "annealed," "quenched," etc., to describe the treatment.¹ Furthermore, the effect of heat treatment is variable and depends on the quality of the steel.²

Magnetic Testing.—That there is a definite relationship between the mechanical and thermal treatment of steel and its magnetic properties has been shown by Robin³ who gives rules and tables of data according to which the composition, thermal and mechanical treatments, of any article of regular shape of steel or nickel alloy can be determined from the characteristic shapes of the magnetic curves. The Bureau of Standards has also done considerable and very valuable work in this field.⁴ This work is so important and of such a nature that the originals should be consulted for the details. The basis of this method of testing is the assumption that for one set of mechanical properties there is one, and only one, set of magnetic characteristics, and vice versa. We know that the hysteresis loss and tensile strength of unhardened steels vary in the same manner, and also that the intensity of magnetization at saturation, the maximum susceptibility and ductility vary in the same way with the carbon content.⁵ Magnetostriction and ductility are also parallel properties,⁶ while the maxima of hysteresis and of tensile strength occur at the eutectoid ratio.⁷

A somewhat different line of investigation was that used by Hanemann and Mercia⁸ who examined the magnetic properties of iron (and nickel) while being loaded and unloaded in a tensile testing machine. One of the main objects of the work, to establish a magnetic definition of the elastic limit, was not accomplished. It was found that "the magnetic induction (and per-

¹ See LANGENBERG and WEBBER, *Trans. Amer. Inst. Min. Eng.*, 1915, Vol. 51, p. 897. See also, GÜMLICH, *Faraday Soc.*, Apr. 23, 1912.

² GÜMLICH and SCHMIDT, *Elektrotechn. Zeit.*, 1901, Vol. 22, p. 691.

³ *Mem. Soc. Ingen. Civil, France*, 1912, Vol. 65, p. 778.

⁴ *Bulletin No. 172*. See also *Trans. A. S. T. M. and Journ. Amer. Steel Treat. Soc.*

⁵ WAGGONER, *Phys. Review*, 1909, Vol. 28, p. 393; and 1912, Vol. 35, p. 58.

Above the eutectoid ratio the intensity of magnetization increases, in contrast to the ductility.

⁶ WAGGONER, *Phys. Review*, 1912, Vol. 35, p. 64.

⁷ WAGGONER, *Loc. cit.* and JONES and WAGGONER, *Proceed. A. S. T. M.*, Vol. 11, p. 492.

⁸ *Trans. Amer. Inst. Min. Eng.*, 1916, Vol. 53, p. 201.

meability) is not dependent upon the previous elastic history of the material, as long as (1) the variations or alterations of stress have been within the elastic limit, and (2) the number of such alternations has been low. It was also concluded that the magnetic method of testing is applicable to the materials examined since the measurements indicated the stress which had been previously applied, provided only that it had exceeded the elastic limit.

The effect of repeated shocks, such as transformer sheets would receive during rail transportation, is that the permeability decreases and the hysteresis loss increases.¹

The Thermo-Electric Properties.—The thermo-electric power of the steels has been measured by various experimenters but the method has not yielded as valuable results as have other methods. Belloc² found a striking similarity in the behavior of the various compositions inasmuch as the " dE/dt vs. t " curves were all similar but displaced to different values for the different amounts of carbon present. The couples used were made of the steel wire and pure platinum.³ The critical point determinations, as made by this method, have not been sufficiently reliable for extended use, for example, Broniewski reports that the e.m.f.—temperature curves show A_2 at 830°C. and A_3 at 950°C. in pure iron. At 0.07 per cent. carbon A_2 is lowered to 850°C. but A_3 is not affected, while A_1 was first noted in the 0.24 per cent. carbon steel.⁴

Electrical Conductivity.⁵—An empirical relationship between the conductivity and composition was established by Benedic⁶ who found that equivalent portions (one dissolved atom per 100 atoms of solution) of added elements, carbon, silicon and manganese, increase the resistance of iron by equal amounts.⁶

¹ See GÜMLICH and STEINHOUSE, *Stahl u. Eisen*, 1913, Vol. 33, p. 147.

² *Annal. Chim. Phys.* 1903, Vol. 30, p. 42.

³ This work has been corroborated by Pecheux, using copper as the neutral element; *Comp. Rend.*, 1909, Vol. 149, p. 1062. Resistivity is also considered in this paper.

⁴ *Comp. Rend.*, 1913, Vol. 156, p. 1983. A considerable amount of information is given by DEPUY and PORTEVIN, *Comp. Rend.*, 1915, Vol. 161, p. 776, and BORDONI, *N. Cimento*, 1913, Vol. 5, Series 6, p. 412.

⁵ The electrical conductivity of iron and many of its alloys was determined by BARRETT, BROWN and HADFIELD, *Proc. Roy. Soc. London*, 1900, Vol. 7, p. 67.

⁶ *Disser. Upsala*, 1904.

increase per dissolved atom is 5.9 microhms per centimeter cube and the resistance of steel is represented by the formula

$$\sigma = 7.6 + 26.8\Sigma C,$$

ΣC being the sum of the equivalent percentages of the elements present, reduced to carbon. Mahler¹ has suggested the formula

$$R = 10 + 7C + 5Mn$$

using Le Chatelier's constants for carbon and manganese. This formula is said to be sufficiently close for use in practice.

Electrical conductivity measurements show marked changes at the critical points but the method can hardly compete with thermal and micrographic analysis.²

One rather novel use of conductivity measurements is that of Portevin who determined the velocity of transformation in steels by this means.³ He found that the increase in resistance, on quenching steel, corresponds to a definite amount of carbon in solution and further that a state of equilibrium is not reached in eutectoid steel by heating ten minutes at 750°C. By extrapolating from a series of quenched steels, the resistance of iron was found to be 9.3 microhms at 20°C.

Specific Heat.—The specific heat has recently been determined by Meuthen.⁴ The specific heat was found to vary as a linear function of the carbon content, but to pass through a maximum at about the eutectoid concentration. The heat effect involved in the pearlite transformation was found to be 15.9 cal. per gm. as compared to 5.6 cal. per gm. for A_2 and 14.1 cal. per gm. for A_3 in pure iron. This maximum is somewhat difficult to explain and has led Tammann to assume that we are dealing with two different kinds of cementite, one which occurs in the eutectoid and one which is found only in hyper-eutectoid steels. The specific heat for low and medium carbon steels is probably between 0.1435 and 0.1440 gram calories for 0° to 650°C.⁵

¹ *Rev. de Metallurgie*, 1905, Vol. 2, p. 345.

² HONDA and SIMIDU measured the electrical and thermal conductivities of a graded series of steels varying in carbon from that of pure Swedish iron to 1.50 per cent. C at temperatures up to 900°C., *Sci. Rep. Tohoku Imp. Univ.*, 1917, Vol. 6, p. 219.

³ *Compt. Rend.*, Vol. 159, p. 51.

⁴ *Ferrum*, 1912-13, Vol. 10, p. 1.

⁵ OBERHOFFER and MEUTHEN, *Metallurgie*, 1908, Vol. 5, p. 573.

Thermal Expansion.—We have already seen that pure iron expands in an anomalous manner at A_2 and that practically no effect is noticeable at A_2 . The same is true with steel, only in addition, there is an effect at A_1 which increases with the carbon content up to a maximum at the eutectoid. Above about 0.6 per cent. carbon it is difficult to distinguish between the A_1 and the A_2 points. The coefficient of expansion decreases as the carbon content increases while manganese also exerts considerable influence in lowering the coefficient.¹ The cementite inversion at 180°C. is brought out by measurements of the thermal expansion.² Thermal expansion curves of quenched steel show irregularities at 400°C. (the osmondite range) and check the results of Heyn and Bauer (Dreisen).

According to the curves given by Driesen the coefficient of expansion between 100° and 200°C. drops from 0.000013 at 0.05 per cent. carbon to 0.000010 at 1.67 per cent. carbon. At temperatures above the critical range the coefficient increases from 0.000020 at 0.09 per cent. carbon to 0.000022 at 0.56 per cent. carbon, and up to 0.000040 at 1.67 per cent. carbon.

IMPURITIES AND FOREIGN INCLUSIONS IN STEEL

So far we have considered principally the influence which carbon has on the properties and microstructure of steel. It is necessary to recognize the fact that commercial steel, as ordinarily produced, contains other substances which may affect the properties and which must be controlled. Some of these substances are in solution and therefore are not visible in steel, and are either additions or impurities, while others are present as separate constituents, produced during the process of manufacture and held mechanically by the steel, and will be called here "foreign inclusions." These two classes of substances, of exceedingly great technical importance, will be considered separately.

Additions and Impurities.—These substances can be subdivided into two classes; (1) those which are harmless (usually desirable) unless present in excess, such as manganese, silicon,

¹ See for example, HONDA, *Sci. Rep. Tohoku Imp. Univ.*, 1917, Vol. 6, p. 203.

² DRIESEN, *Rev. de Met.*, 1917, Vol. 14, p. 683. DRIESEN found the critical points as determined by thermal expansion to agree closely with those found by the usual methods of thermal analysis.

and copper and (2) those which are dangerous unless present in very small amounts, such as phosphorus, nitrogen, hydrogen and other gases.

Manganese.—Manganese comes directly after carbon in importance as a constituent of commercial steel. The reasons for its great technical importance may be summed up in a statement of the functions of manganese taken from a report, by the author, of a research conducted by the Bureau of Mines and the National Research Council.¹

The first function of manganese, broadly considered, is to refine and settle up the molten bath of steel. The aim is to put the metal in a proper condition for pouring and to produce ingots (or castings) of the desired quality and texture. While other elements are more effective and efficient, manganese is the most satisfactory element that can be used for this purpose on account of the excellent condition, from the point of view of freedom from objectionable foreign inclusions, which it imparts to the bath. Manganese is also desirable in steel to improve the rolling properties, in which capacity it appears to serve a dual purpose. First the manganese deoxidizes and refines the molten steel in such a way as to give ingots of the desired texture without robbing the steel of its hot working properties. Such ingots may be rolled into the finished shape without the formation, in excessive amount, of fissures or surface defects. Other reducing agents, such as aluminum, silicon, etc., are prone to leave the metal in a poor condition for rolling and forging; while they eliminate one cause of hot shortness, iron oxide, they fail to convert the sulphur into a harmless form, as does manganese, and leave behind their highly refractory oxides, both of which tend to produce poor rolling qualities. Secondly, manganese by retarding the rate of coalescence, or grain growth, renders steel less sensitive to the effects of high rolling temperatures and it is also supposed to promote plasticity. Silicon and aluminum, on the other hand, increase rather than decrease the grain size of steel. For these reasons, manganese in amounts varying between about 0.4 and 0.7 per cent. is used in the common grades of steel ranging in carbon content up to that of rail steel.

The minimum amount of manganese required in ordinary Bessemer and open hearth practice varies considerably with the condition of the steel at the time the manganese addition is made.

¹ *Bull. Amer. Inst. Min. Eng.*, No. 146, 1919, p. 277.

If the heat is well made and reasonably free from oxidation, as little as 0.35 to 0.4 per cent. would undoubtedly suffice. In order to insure sufficient deoxidation in all cases, the finished steel is generally made with 0.5 to 0.7 per cent. manganese. The maximum amount of manganese which should be allowed is not as definitely known but it probably decreases as the carbon content increases. For example, 1 per cent. manganese would be too much for rail steel which contains 0.6 to 0.8 per cent. carbon, this amount of manganese being sufficient to increase the brittleness to the danger point.

Finally, manganese is desired in the finished steel to secure certain physical or mechanical properties or to make the steel more amenable to subsequent heat treatment. For a medium carbon forging steel, the manganese content is usually about 0.60 per cent. While this amount of manganese is sufficient to insure a satisfactory heat treatment, it is strongly believed that steel containing 1 to 1.5 per cent. manganese, on account of its superior qualities when heat treated, should be more extensively employed. In such "low manganese steels" the carbon content will be somewhat lower than the amount which would ordinarily be required to produce the same strength. The figures in Table 63 are added to illustrate this point.¹

TABLE 63.—EFFECT OF MANGANESE ON THE MECHANICAL PROPERTIES OF STEEL

Composition		Treatment	Y. P., lb. per sq. in.	T. S., lb. per sq. in.	Elong., per cent.	R. A., per cent.	Charpy test mkg.	Brinell hard- ness No.
C	Mn							
0.109	0.285	Hot rolled.....	46,000	62,500	27.8	53.5	23.5	119
		Annealed.....	43,000	57,000	31.5	70.0	30.8	113
		Quenched.....	43,000	79,000	19.6	61.0	23.6	146
0.126	0.675	Hot rolled.....	50,000	66,500	29.4	63.9	28.1	115
		Annealed.....	44,000	59,500	30.2	70.0	31.0	115
		Quenched.....	48,500	84,000	16.0	62.0	29.4	154
0.098	1.020	Hot rolled.....	51,500	68,000	28.6	64.2	31.8	123
		Annealed.....	45,500	61,000	30.7	71.8	37.2	123
		Quenched.....	54,000	97,000	15.5	53.0	27.2	179
0.101	1.315	Hot rolled.....	54,000	71,000	28.0	67.7	34.0	134
		Annealed.....	47,500	66,000	29.8	70.3	44.0	135
		Quenched.....	66,000	111,000	16.3	47.8	18.1	237

Quench: 1 hr. at 900°C., water at 15°C. Anneal: 1 hr. at 900°C., kieselguhr.

¹ LANG, *Metallurgie*, 1911, Vol. 8, pp. 15 and 49.

The material was rolled, annealed and quenched according to standard practice. Elongations were measured on a gage length equal to ten times the diameter. The toughness was measured on a 75 mkg. Charpy testing machine and the hardness number is the Brinell ball hardness number.

The increase in strength and toughness combined with a comparatively small decrease in ductility, produced by the addition of manganese, is noteworthy. Manganese increases the hardness somewhat and the hardening capacity to a greater extent, which can be explained as due to its retarding influence on the transformations during quenching and the consequent production of martensite. This influence of manganese is brought out clearly in the photomicrographs. Lang states that the ratio of the Brinell hardness to the tensile strength in these tests varied by as much as ± 20 per cent. so that the tensile test could hardly be replaced by the Brinell test.

According to Lang's tests, manganese raises the coercive force and hysteresis and lowers the permeability while the remanent magnetism remains practically constant. This effect is particularly noticeable in the quenched steels. The electrical resistance (of 1 c.cm.) is raised by 5.5 microhms by 1 per cent. manganese which agrees with the figures of Le Chatelier,¹ Benedicks,² and Burgess and Aston.

In mild steel, it is clear from these figures that over 1 per cent. manganese is desirable for many purposes but especially so if high notch toughness is required. On the other hand, the manganese should be low for good magnetic and electrical properties.³

¹ Contribution a l'Etude des Alliages, p. 416, (1901).

² *Zeits. phys. Chemie*, 1902, Vol. 11, p. 545.

³ The above opinion as to the efficacy of increasing the manganese content and lowering the carbon content is not at all unanimous. For example, HARBORD (*Metallurgy of Steel*, 1916, p. 374) gives it as his opinion that "for mild steel and rail steel the less manganese a steel contains above that required to insure solid ingots and freedom from red shortness the better" and that there should be little difficulty in obtaining these results with 0.4 to 0.5 per cent. Mn in the finished steel in good open hearth practice. He also points out that up to 1 per cent. Mn is allowable in good axle and tire steel as it does not dangerously reduce the ductility and toughness but that for mild steel, boiler plate, and structural steel, manganese above 0.6 per cent. begins to be dangerous and he deprecates the tendency among steel makers to increase the tensile strength by increasing the manganese rather than carbon. It might be stated here that the use of carbon or of manganese to improve the strength of steel seems to depend upon the condition

Manganese is used in high carbon steels to increase their hardness when quenched. Manganese at the same time increases the tendency of these steels to crack or check on quenching, so that the manganese must be held to within rather narrow limits. 0.2 per cent. manganese is the minimum amount of manganese which will produce the proper hardness while more than 0.4 per cent. manganese would be excessive. Ordinarily about 0.25 to 0.30 per cent. manganese is used in high grade tool steel.

Silicon.—Silicon is used in steel making practice for two reasons, sometimes for one, sometimes for the other, and sometimes for both. First of all, silicon is a powerful reducing agent, and, like manganese, is added to the molten steel to "settle up" the bath. In this respect it is very powerful, more so than manganese, but the oxidation product, SiO_2 , must be given considerable time to leave the bath. Secondly, silicon acts in such a manner that the dissolved gases, hydrogen, nitrogen, etc., are held in solution during solidification and the resulting ingots or castings are "solid." In this latter respect silicon behaves differently from manganese which seems to have but little effect on the dissolved gases.

On the other hand, the influence of silicon, in the amounts commonly found (*i.e.*, under 0.15 per cent.), on the common properties of steel is negligible.¹ Silicon in larger amounts, for example 1 per cent., increases the tensile strength of the forged alloys from 45,000 lbs., for vacuum fused iron to 60,000 lbs., and of the annealed (970°C.) alloys from 35,000 lbs. to 46,000 lbs. The ductility remains fairly constant. This is corroborated by the work of various investigators.²

in which the steel is to be used. Thus, if the steel is in the form of structural shapes and other non-heat-treated parts, it would seem best to use carbon as the strengthening agent; on the other hand, if the properties, such as strength, toughness, etc., are to be secured in the finished product by means of heat treatment it would seem best to do so by increasing the manganese.

¹ CAMPBELL, *The Manufacture and Properties of Steel*, 1907.

² See YENSEN, the University of Illinois Expt. Station, *Bull.*, No. 83, 1915. A constitution diagram of Fe-Si is given by YENSEN which shows the probable influence of silicon on A_2 and A_1 . HADFIELD, *Journ. Iron and Steel Inst.*, 1889, No. 2, p. 222. BAKER, *Ibid.*, 1903, No. 2, p. 312. PAGLIANTI, *Metallurgie*, 1912, Vol. 9, p. 217. CAMPBELL, "The Manufacture and Properties of Steel," 1907. One instance of the utility of adding silicon to plate steel has been given to the writer (private communication). In this case a tensile

The well known effect of silicon on the magnetic properties of iron will be considered under "Silicon Steel," the name which has been given this alloy. 1 per cent. silicon was found by Burgess and Aston¹ to raise the resistance of electrolytic iron from about 12.5 microhms per centimeter cube to about 24 microhms.

The effect of silicon on the transformations of pure iron is not as yet cleared up, but the solubility of silicon in α , β , and γ iron is indicated by the fact that the transformations occur over intervals of temperature. According to Osmond and Baker, A_1 is lowered about 8°C. by 1 per cent. silicon and the pearlite point is shifted to the left. Charpy and Cornu-Thenard state that silicon diminishes A_3 in intensity and raises its temperature, and that A_2 falls and A_1 rises with increase in silicon.² The influence of small amounts of silicon is practically negligible; however, the subject will be further considered under "Silicon Steel."

In the presence of carbon (*i.e.*, in steel) silicon has the same general effect as given above for pure iron, but when present in the amounts usually found in well-made steel (up to 0.3 per cent.) its effect on the strength and ductility is negligible.³ In greater amounts, silicon raises the yield point, tensile strength and hardness but lowers the elongation and reduction of area of untreated, annealed and quenched steels,⁴ according to Paglianti, but the resistance to bending of notched bars is not changed up to 1.4 per cent. silicon. A summary of his results is given in Table 64.

The influence of silicon on the welding properties of low carbon steel does not seem to be thoroughly understood. According to some authorities (Turner and Hadfield), silicon has no injurious effect on the working of steel, either hot or cold, and when it is present in the usual amounts, the same is true of welding. In technical practice, however, it is generally held that the presence of silicon in steel for tubes, etc., which must be welded, is decidedly injurious.

strength of 80,000 lbs. per sq. in. in $1\frac{1}{4}$ inch plate was required. This was secured, without lowering the ductility, by increasing the silicon to raise the strength, and by lowering the carbon to keep the ductility constant.

¹ *Met. and Chem. Eng.*, 1910, Vol. 8, p. 133.

² *Journ. Iron and Steel Inst.*, 1915, No. 2, p. 276.

³ See TURNER, Report of the Committee appointed by the British Association 1888, and HADFIELD, *Loc. cit.* These results are corroborated by the author's private notes.

⁴ C = 0.12 to 0.15 per cent.

TABLE 64.—EFFECT OF SILICON ON THE MECHANICAL PROPERTIES OF STEEL

Composition			Lbs. per sq. in.		Elong., per cent.	R. A., per cent.	Notch tough., mkg. per sq. cm.	B. H. No.	Sp. gr.
C	Si	Mn	Y. P.	T. S.					
0.12	0.24	0.41	45,515	62,600	30.0	57.5	26.7	130	7.861
0.10	0.37	0.30	47,600	61,160	29.5	67.0	36.0	131	7.853
0.11	0.67	0.23	49,300	65,000	28.3	58.0	34.2	144	7.835
0.11	0.95	0.36	53,700	68,980	28.2	55.0	31.5	150	7.810

Material cast into 100 mm. square ingots and rolled into 32 mm. round rods

0.12	0.24	0.41	38,402	55,600	27.5	67.5	21.0	118	
0.10	0.37	0.30	40,600	56,570	27.3	69.5	21.2	122	
0.11	0.67	0.23	45,200	61,400	26.0	68.7	20.3	126	
0.11	0.95	0.36	45,200	62,800	21.5	64.5	19.7	136	

32 mm. round rods, annealed 10 hours at 1100°C. and slowly cooled

0.12	0.24	0.41	52,000	81,500	17.5	65.2	31.2	162	
0.10	0.37	0.30	61,160	89,000	16.7	58.6	30.5	187	
0.11	0.67	0.23	64,000	96,400	15.6	57.6	29.5	205	
0.11	0.95	0.36	64,000	99,562	14.8	55.0	23.8	210	

32 mm. round rods, annealed one hour at 900°C. and quenched in water at room temperature.

Inasmuch as silicon goes into solution in ferrite, the change in grain size is the only apparent change in the microstructure produced by the addition of silicon to low carbon steel. The effect of silicon on medium and high carbon steels will be considered later.

Phosphorus.—With the exception of Swedish ore (and possibly Brazilian ore) it may be stated that phosphorus is always found in our commercial iron ores. This phosphorus is reduced in the blast furnace and is present in greater or lesser amounts in the finished steel. The presence of this phosphorus is held to be prejudicial to the quality of the steel and the desire is to keep it below a certain specified maximum amount.¹ This attitude towards phosphorus in steel has led to considerable investigation as to its behavior in and its effect on the properties of steel. For most of our information in this very important field we have to thank Dr. J. E. Stead who has summarized his more important

¹ Certain exceptions to this will be considered.

results in three papers to the Iron and Steel Institute, which are profusely illustrated with photomicrographs.¹

Stead came to the conclusion that phosphorus occurs in iron and steel in the form of Fe_3P which is soluble in iron at the freezing point to 1.7 per cent. These two facts have since been verified by Le Chatelier and Wologdine² and Saklatwalla³ and Gercke.⁴ It follows then that phosphorus in commercial steel is always present in solution, and on that account it has been necessary to develop special etching reagents in order that the distribution of phosphorus in steel might be shown microscopically.⁵

Stead has shown that this phosphorus possesses three very harmful characteristics—(1) that it segregates badly on solidification, (2) that it persists in the segregated state through very slow diffusion, even if the steel is worked at high temperature, and (3) that it causes coarse crystallization. These three characteristics result in the formation of hard, coarse grained, and brittle ferrite segregations in forgings and rolled sections which are not eliminated in commercial practice and which frequently lead to premature failure.⁶ This is the “cold shortness” which is commonly caused by phosphorus, and is particularly in evidence at low temperatures. A typical case of gross phosphorus segregation in mild steel is shown in Fig. 94.

The effect of phosphorus in steel increases greatly as the carbon content increases. In wrought iron and low carbon steel phosphorus generally does no material harm unless it runs very high— >0.3 per cent. In fact Stead cites certain grades of wrought iron containing 0.4 per cent. to 0.5 per cent. phosphorus which are better for structural purposes than the best Swedish wrought iron; in fact they are stronger and more easily welded. In sheet bar steel the phosphorus is allowed to run up to 0.10 per cent. to prevent welding or sticking of the packs during rolling. In certain other steels phosphorus is purposely added to improve

¹ *Journ. Iron and Steel Inst.*, 1900, No. 2, p. 60; 1915, No. 1, p. 140; and 1918, No. 1, p. 389.

² *Compt. Rend.*, 1909, Vol. 149, p. 709.

³ *Metallurgie*, 1908, Vol. 5, p. 331; *Journ. Iron and Steel Inst.*, 1908, No. 2, p. 92.

⁴ *Metallurgie*, 1908, Vol. 5, p. 604.

⁵ See Part I for these etching methods.

⁶ “Ghost lines,” as the segregations have been termed, both with and without slag inclusions, will be considered a little further on.

the cutting properties. In other grades of mild steel the phosphorus is kept well under 0.10 per cent.

The first systematic attempt to determine the particular effect of phosphorus on mild steel is that of d'Amico who determined the properties of a graded series of steels ranging from 0.012 per cent. to 1.24 per cent. phosphorus.¹ The original steel contained carbon 0.118, manganese 0.400, silicon 0.247, sulphur 0.051, phosphorus 0.012. Its properties were T. S., 60,000 lbs., Y. P., 45,200 lbs.; E. L., 29,868 lbs.; Elong., 28 per cent.; R. A., 61.5 per cent. The conclusions drawn were as follows. (1) The hardness



×1.3

FIG. 94.—Phosphorus segregation in a mild steel rod. Etched with copper-ammonium chloride. (Hanemann.)

increases uniformly by about 12 units on the Brinell scale for each 0.1 per cent. phosphorus; (2) the elastic limit (Martens mirror extensometer) was likewise raised by 3,830 lbs. per sq. in.; (3) the tensile strength is raised to a maximum at about 0.5 per cent. phosphorus by 6,540 lbs. per sq. in. for each 0.1 per cent. phosphorus; (4) the elongation is lowered by about 1 per cent. for each 0.1 per cent. phosphorus up to 0.6 per cent. phosphorus and then more rapidly with further increase in phosphorus; (5) the reduction of area is lowered by 4 per cent. for each 0.1 per

¹ *Ferrum*, 1913, Vol. 10, p. 289.

cent. phosphorus up to 0.6 per cent. phosphorus and then more rapidly with further increase in phosphorus; (6) the notch toughness (Charpy test) decreases rapidly from about 35 mkg. per sq. cm. to zero as soon as the phosphorus exceeds 0.25 per cent.; (7) the electrical resistance increases by 0.11 ohms for each 0.1 per cent. phosphorus measured on a wire one meter long with a cross sectional area of one sq. mm.; (8) the permeability was little affected by the addition of phosphorus (annealed material) up to 0.5 per cent.; (9) the hysteresis loss is also little affected by phosphorus and the author remarks that the presence of phosphorus in electrical steels has little technical interest.

A practical demonstration of the fact that phosphorus can replace carbon in low carbon steel without detriment to the steel (Stead) is to be had in the recent work of the Carnegie Steel Company.¹ For the purposes of these tests a series of ingots with varying phosphorus content was made in the usual manner and made into the finished parts (rivets, nails, barrels, automobile parts, etc.) according to current shop practice. The acid open hearth steel base analyzed carbon 0.12 per cent.; manganese 0.36 per cent.; phosphorus 0.032 per cent.; sulphur 0.036 per cent.; silicon 0.020 per cent.; copper 0.014 per cent.; while the basic open hearth base analyzed carbon 0.12 per cent.; manganese 0.36 per cent.; phosphorus 0.008 per cent.; sulphur 0.037 per cent.; silicon 0.022 per cent.; copper 0.012 per cent. The phosphorus content of the ingots used is given in Table 65. Tensile tests were made on sheet bar 0.467 inch thick and on one inch round bars. These tests are reproduced in Table 65.

In the practical tests it was found that all of the steels could be worked into finished shape, or that, in other words, none of the steels was found to be brittle on account of the phosphorus. The principal effect of the phosphorus was the increase in strength and hardness so that while the phosphorus would not necessarily be harmful, it would not be a desirable constituent on account of the greater difficulty of working the high phosphorus material. Dr. Unger suggests decreasing the carbon content to offset the increase in phosphorus.

Phosphorus in medium carbon and forging steel is generally kept below 0.04 per cent. principally because, by lowering the total phosphorus present, the liability of the phosphorus to segregate is lessened. Stead has accumulated the following data on the

¹ UNGER, *Trans. Amer. Iron and Steel Inst.*, 1918.

effect of the addition of phosphorus to steel containing 0.30 per cent. carbon.

TABLE 65.—EFFECT OF PHOSPHORUS ON THE MECHANICAL PROPERTIES OF 0.12 PER CENT. C STEEL

Tensile Tests on Sheet Bar .467" thick. Longitudinal

Kind of steel	Per cent. P	Elastic limit, lb. per sq. in.	Tensile strength, lb. per sq. in.	Elongation, per cent. 8 in.	R. A., per cent.
Acid O. H.....	.032	30,750	54,280	29.3	58.7
Acid O. H.....	.058	31,215	57,290	32.0	58.7
Acid O. H.....	.085	33,120	59,200	30.6	57.1
Acid O. H.....	.115	35,665	62,070	29.4	47.0
Basic O. H.....	.008	29,130	50,780	34.3	61.0
Basic O. H.....	.030	30,405	51,940	32.4	63.2
Basic O. H.....	.052	30,675	54,350	32.4	62.6
Basic O. H.....	.080	30,540	55,820	31.2	56.8
Basic O. H.....	.110	32,550	58,635	31.2	55.9

Tensile Tests on 1" Rolled Rounds. Untreated

Acid O. H.....	.032	39,910	55,450	26.8	66.5
Acid O. H.....	.058	40,130	56,880	25.0	64.2
Acid O. H.....	.085	41,540	59,640	26.2	64.0
Acid O. H.....	.115	42,900	60,640	26.0	65.9
Basic O. H.....	.008	34,410	49,350	28.7	71.6
Basic O. H.....	.030	37,350	51,380	29.0	70.9
Basic O. H.....	.052	38,060	52,240	28.3	70.3
Basic O. H.....	.080	40,530	55,840	27.5	70.3
Basic O. H.....	.110	40,180	57,000	23.7	60.2

TABLE 66.—EFFECT OF PHOSPHORUS ON THE MECHANICAL PROPERTIES OF 0.3 PER CENT. C STEEL

Per cent. P	Yield point, lb. per sq. in.	Tensile strength, lb. per sq. in.	Elongation, per cent. 6 in.	R. A., per cent.	Revolutions to fracture ¹	Ratio
0.040	45,696	74,000	23.0	52.0	61,085	1.0
0.300	56,896	89,300	23.0	45.3	167,690	2.74
0.500	71,680	99,000	20.0	45.3	651,490	10.65

The phosphorus content has been allowed to run up to 0.08

¹ Woehler test.

per cent. even in hard forging steel in order to secure the increased yield point. On the basis of Stead's figures, it can be seen that the addition of small amounts of phosphorus to 0.3 per cent. carbon steel, excepting for segregation, is less harmful than a corresponding increase in carbon would be. It is when the phosphorus exceeds 0.07 per cent. that its harmful characteristics become readily apparent, and when it exceeds 0.09 per cent. the effect is very pronounced.¹ This effect is to coarsen the structure and to isolate the ferrite grains and the pearlite colonies, rendering the material brittle and increasingly more difficult to beneficiate by heat treatment. Unless the phosphorus is too high (>0.07 per cent.) a uniform structure, with considerable ductility, can be secured by quenching from above A_c , followed by a draw. This treatment, however, does not necessarily produce a uniform distribution of the phosphorus.

The effect of phosphorus on high carbon or tool steel is held to be very dangerous and it should not be over 0.025 per cent. in the best steels. According to Stead, phosphorus makes high carbon steel fine grained, although phosphorus has the very decided influence of throwing off the carbon after solidification has taken place and therefore one would expect to find the effect of phosphorus practically limited to the ferrite, which it coarsens.²

Microscopic Study of Phosphorus in Steel.—This feature will be considered a little further on under "Ghost Lines in Steel."³

Thermal Critical Points.—The effect of phosphorus on the critical points of steel has not been definitely worked out. It is assumed by Edwards that phosphorus raises the critical points of steel, in fact the formation of carbon-free, high-phosphorus bands (ghost lines) is generally based on such an effect. Haughton and Hanson, contributing to the discussion of Stead's 1918 paper stated that the A_2 point is lowered to 740°C. by the addi-

¹ DE KRYLOFF, *Rev. de Metallurgie*, 1908, Vol. 5, p. 355.

² This repulsion of carbon from phosphorus has been thoroughly considered by STEAD. The writer had opportunity to test this phenomenon during the microscopic examination of a German H.E. shell fragment. The steel contained 0.16 per cent. P and was cast, so that the dendritic structure was very apparent. The phosphorus was found to be at those parts corresponding to the interstices of the original dendrites while the carbon or pearlite occupied those portions which must have been the dendrites proper.

³ See the papers by STEAD; also ROSENHAIN and HAUGHTON, "A New Etching Reagent for Mild Steel," *Journ. Iron and Steel Inst.*, 1914, No. 1, p. 515.

tion of 1.9 per cent. phosphorus. A positive statement as to the effect of phosphorus on Ar_3 is much to be desired. Thermal analysis of the German H.E. shell fragment showed that both Ac_1 and Ar_1 are raised, Ac_1 to 760°C. and Ar_1 to 702°C., although the shell contained 0.56 per cent. silicon, the carbon being 0.6 per cent., and the manganese 0.57 per cent.

Copper.—The influence of copper when present in more than normal amounts (*i.e.*, over 0.5 per cent. copper) will be considered under "Copper Steel." Copper in small amounts apparently has a negligible effect.¹ It has been said that copper produces red shortness and, on this account, copper has been regarded as an undesirable constituent in steel. This theory has recently been disproved and it is now held that copper up to 0.50 per cent. is, if anything, a desirable constituent in steels. Stead² has done considerable to remove the prejudice against copper. He showed that copper retards somewhat the formation of pearlite so that the carbide is more diffused and that copper increases the tensile strength and elastic limit and slightly decreases the elongation and reduction of area. In compression, bending and welding tests there was no difference between the copper and the non-copper steels although the steels containing copper were somewhat more sensitive to high temperatures.

Campbell³ states that structural steel produced by the Pennsylvania Steel Company contains up to 0.35 per cent. copper and that no injurious effects have been noticed due to its presence. These conclusions have been verified by Dillner⁴ who found the tensile strength to increase and the elongation to decrease in proportion to the amount of copper present.

This beneficial, or at least harmless, effect of copper is evidently limited to steels containing only smaller amounts of carbon and copper as Stead and Wigham⁵ showed that copper up to 2 per cent. is of more harm than good in high carbon steel wire. Further verification is to be had in a later report by Wigham⁶ which brought out, among other things, that steel with

¹ Probably the single exception to this is the effect of copper up to 0.2 per cent. on the atmospheric corrosion of mild steel.

² STEAD and EVANS, *Journ. Iron and Steel Inst.*, 1901, Vol. 1, p. 89. STEAD, *The Metallographist*, 1902, Vol. 5, p. 25.

³ *The Metallurgy of Steel*, 1896, p. 276.

⁴ *Stahl u. Eisen*, 1906, Vol. 26, p. 1493.

⁵ *Journ. Iron and Steel Inst.*, 1901, No. 2, p. 122.

⁶ *Iron and Steel Inst. Carn. Sch. Rep.*, 1906, Vol. 69, No. 1, p. 222.

0.25 per cent. copper, with high carbon (0.70 per cent.) with or without a high percentage of manganese, gave a good wire. He considered it to be proved that copper to the extent of 0.25 per cent. is no disadvantage in the manufacture of the best class of steel wire.

Copper has been found to be without harmful effect on the magnetic properties of transformer sheets.¹

Copper has about the same effect on the critical points as manganese and nickel, and, according to Breuil,² its effect in low carbon steel is to diminish Ar_1 in magnitude and to lower Ar_2 ; in medium carbon steel, its effect is to lower Ar_1 . In high carbon steel Ar_1 is considerably below normal and remains practically constant between 575° and 600°C. for a variation in copper from 0.5 per cent. to 2.0 per cent.

Arsenic.—The experience with arsenic, at least when it is present in small amounts, seems to be that it is quite neutral in its effects on steel, and it may be assumed that arsenic up to 0.17 per cent. has no effect on the properties of steel in the cold state.³ Arsenic up to 1 per cent. does not produce red shortness but as little as 0.25 per cent. is sufficient to prevent welding. These conclusions have been confirmed by Stead⁴ and Marshall⁵ who noted that in all cases when arsenic exceeded 0.2 per cent. it was necessary to use a flux in welding. Liedgens⁶ conducted a systematic investigation of a series of sixteen steels containing 0.08 per cent. carbon and up to 3.5 per cent. arsenic and found that arsenic increases the strength, brittleness, specific gravity, and electrical resistance of steel. The hysteresis and coercive force were first influenced favorably by adding arsenic while magnetizability and remanent magnetism remained unaffected. He concluded that arsenic in small amounts is neither harmful nor beneficial.

Tin.—Tin apparently is not a desirable constituent in steel, and yet, like arsenic, when present in small amounts it does not seem to be detrimental.⁷ At least 0.5 per cent. must be present before forging and working properties are affected al-

¹ BURGESS and ASTON, *Electrochem. and Met. Indus.*, 1909, Vol. 7, p. 527.

² *Compt. Rend.*, 1906, Vol. 142, p. 1421, and Vol. 143, p. 346.

³ HARBORD and TUCKER, *Journ. Iron and Steel Inst.*, 1898, No. 2, p. 183.

⁴ *Journ. Iron and Steel Inst.*, 1895, No. 1, p. 108.

⁵ *Bull. de la Soc d' Encourage.*, 1898, p. 1336.

⁶ *Stahl u. Eisen*, 1912, Vol. 32, p. 2109.

⁷ LEDEBUR, *Stahl u. Eisen*, 1901, Vol. 21, p. 330.

though smaller amounts are detrimental to welding. The principal source of tin in steel is detinned scrap, but there is hardly sufficient information at present as to the effect of tin in small amounts to permit placing a limit on the tin content of the scrap.

Aluminum, Titanium, Zirconium and Cerium.—These metals are added to steel to assist or to complete the deoxidizing action of manganese, and also to improve the "condition" of the steel. When used in this manner their action is similar to that of silicon only unlike silicon, their presence is not desired in the finished steel. The behavior of these elements will be considered in detail in Part III.

Gases in Steels.—It has long been known that steels absorb gases during the process of manufacture and that these gases are retained even after solidification and cooling to room temperature. The exact effect of these gases on the properties of steel is still a matter of discussion although the quite logical assumption is that the better grades of steel contain smaller amounts of gas than the poorer grades. Certain measurements supporting this statement will be discussed later.¹

On the other hand, steel as it is ordinarily made and treated, probably does not contain much gas and, at present, it would be assuming too much to say that the difference in quality between the various grades of steel is due to differences in the amounts of gas they contain. This is due principally to inaccuracies in our analytical methods of determining the gases in steel and, up to the present, to our lack of reliable results with which to compare one steel with another.² Our principal interest in gases in steel, at this place, is in the effect of gases on the properties of steel, while at another place we shall consider gases and their effect on the refining and "condition" of steel.

¹ A somewhat conflicting statement is that of HEROULT, that the quantity of the gas contained in steel varies but little with the method of manufacture and that small amounts are not injurious. *Trans. Amer. Electro-Chem. Soc.*, 1910, Vol. 17, p. 135, and *Met. and Chem. Eng.*, 1910, Vol. 8, p. 332.

² This entire subject is now being taken up by Dr. J. R. CAIN of the Bureau of Standards and reference should be made to the reports which are issued from time to time. Dr. CAIN has shown, among other things, that two of the common errors in previous work are due to failure to extract all the gases and to reactions which take place during the "run" which affect the amounts of the various gases present. It is believed that methods will be worked out which will give a true comparison of the gas content of different steels.

The early method of extracting gases from steel for the purposes of analysis was to drill the steel under some liquid such as water and to collect the gases given off. It was found later, however, that a better method of extracting the gases was that of heating the steel *in vacuo*. In this way Baker¹ and Baraduc-Muller² determined the gases given off by some of the technical grades of iron and steel. Baker found that crucible steel (0.9 per cent. carbon) on being heated to 800°C. gave off 1.34 cubic centimeters of gas per gram. A sample of soft steel gave off 0.81 cubic centimeters and after rolling, 0.4 cubic centimeters. On determining the gases given off at successively increasing temperatures, it was found that hydrogen was the first given off, between 500 and 600°C. Above this temperature, carbon dioxide and carbon monoxide and finally nitrogen, were given off. No evidence of a dissociation pressure was obtained and so it was concluded that gases were simply occluded or in solution, but it was found that the chief evolution of gas occurred at the critical points while the steel was undergoing its transformation. Finally, he found no relation between the amount of carbon monoxide and the amount of carbon in the steel.

These findings are essentially the same as those of Belloc,³ who pointed out further that at temperatures above 550°C., carbon dioxide is reduced by hydrogen. In a later paper⁴ he concluded that there is a direct connection between the evolution of gas and the critical points, which indicates that while the atoms are rearranging themselves, the steel loses its hold, at least temporarily, on the gases in solution.

Contrary to the findings of Baker, Austin⁵ concludes that the relative amounts of gas in different steels and cast iron increase with the carbon, although cast iron contains relatively smaller amounts of gas. Austin introduced an improvement in the analytical method in that the sample was heated to the fusion point in each case. The figures in Table 67 are taken from Austin's work.

¹ *Carn. Sch. Mem.*, 1911, Vol. 3, p. 249.

² *Ibid.*, 1913, Vol. 6, p. 216.

³ *Rev. de Mét.*, 1908, Vol. 5, p. 469; *Compt. Rend.*, 1907, Vol. 145, p. 1280; and 1908, Vol. 147, p. 244.

⁴ *Bull. de la Soc. d'Encour.*, Vol. 110, p. 492.

⁵ *Journ. Iron and Steel Inst.*, 1912, No. 2, p. 236.

TABLE 67.—GAS ANALYSES OF STEEL

Material	Chemical analysis					Gas analysis			Cubic cent. per gram
	C	Si	Mn	S	P	CO ₂ Vol. per cent.	CO Vol. per cent.	H ₂ , N ₂ etc., Vol. per cent.	
1. Cast iron.....	3.50	2.50	0.60	0.05	1.50	3.1	23.0	73.9	0.24
2. Crucible steel.....	1.10	0.24	0.39	0.02	0.02	0.4	44.2	55.4	1.73
3. Medium-carbon steel....	0.49	0.35	0.72	0.02	0.02	0.6	45.1	54.3	1.35
4. Open-hearth steel.....	0.09	0.05	0.75	0.05	0.05	5.6 ^a	31.5	62.9	0.66
						0.7 ^b	43.0	46.3	0.31
5. Bessemer steel.....	0.05	0.09	0.29	0.06	0.05	5.2 ^a	59.8	35.0	0.97
						3.8 ^b	43.5	52.7	0.87

^a = Gas given off during first heating period.

^b = Gas given off during second heating period.

Sieverts has conducted a series of experiments on gases and metals which throws some light on the question.¹ He found

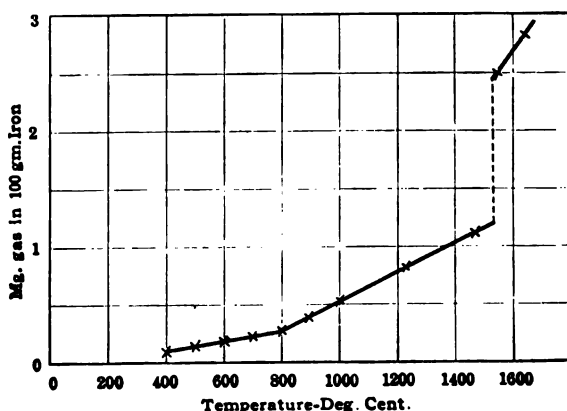


FIG. 95.—Solubility of hydrogen in iron. (Sieverts.)

that the diffusion of hydrogen in iron begins at 400°C. and increases with the temperature. Nitrogen is slightly absorbed at 900°C. but no diffusion was noted at 1000°. This gas is not given off again at 500°C. in a vacuum, but is evolved at 900° and above due, presumably, to the change to γ iron. He showed further² that annealing iron in hydrogen at atmospheric pressure and at temperatures up to 920°C. had no effect on the electrical

¹ Zeit. physik. Chemie, Vol. 60, p. 129.

² Intern. Journ. Metallography, 1912, Vol. 2, p. 37.

conductivity, although iron is one of the hydrogen-dissolving metals. He found¹ that carbon monoxide and hydrogen dissolve in iron above 1000°C. and that the solubility increases with the temperature, being greater in the liquid state than in the solid. This is shown for hydrogen in Fig. 95. This sudden change in solubility on solidification is of great technical importance and will be considered in Part III under Casting Practice.

The early work of Goerens² is also subject to experimental error inasmuch as he failed to fuse the sample. It will be interesting to see if his conclusion that the process of deoxidation leads to a higher gas content in the steel will be substantiated by future work. This is shown by Table 68.

TABLE 68.—EFFECT OF DEOXIDATION ON GASES IN STEEL

Basic Bessemer steel	C.cm. of gases in 1 c.cm. of steel				
	H	CO	CO ₂	N	Total
After blowing; before deoxidation.....	0.22	0.56	0.10	0.03	0.91
After blowing; after deoxidation.....	0.20	2.55	0.24	0.36	3.38

This increase may be due to gas contained in the ferromanganese used and to a reaction between the carbon of the ferromanganese and iron oxide in the steel. Goerens showed, in fact, that 'oxidized' steel and cast iron, both of which had been heated in vacuo, when heated in intimate contact with each other, evolve considerable quantities of carbon monoxide.

More recently Goerens and Paquet³ made use of the method adopted by Wüst to determine carbon in steel of first dissolving the sample in a molten alloy of three parts antimony and one part tin.⁴ This was done to secure a more complete and reliable extraction of the gases contained in the sample, although the temperature employed was only 1150°C. Some of the results obtained by using the new method are reproduced.

The total gas (CO₂ + CO + H + N) was found to vary considerably for equal amounts of carbon, manganese, silicon, phosphorus and sulphur. The smallest amounts of gas were found

¹ *Zeit. f. Electrochem.*, 1910, Vol. 16, p. 707.

² *Intern. Cong. of Mining and Metallurgy, DUSSELDORF, 1910. Division of Theoretical Metallurgy*, p. 64. Also *Metallurgie*, 1910, Vol. 7, p. 384.

³ *Ferrum*, 1915, Vol. 12, p. 57.

⁴ WÜST, *Metallurgie*, 1910, Vol. 7, p. 321.

in low carbon electric steel. Well "settled up" steel was found to contain 10 to 15 cubic centimeters of gas per 100 grams—see 8 and 9. Electric steel with more carbon contains more gas but the increase is not proportional to the carbon content. Poorly treated steel showed twice as much gas as the properly handled material—see 18 and 20. The crucible steel examined unfortunately was of inferior quality. This was especially so with No. 26 which was known to be exceptionally poor.

TABLE 69.—GAS CONTENT OF TECHNICAL GRADES OF STEEL

No.	Composition						c.c. gas per 100 gm.	Weight, per cent.					
	C	Mn	P	S	Si			CO ₂	CO	H	N	Total	
Basic Bessemer Steel													
1	0.05	0.36	0.110	0.045	22	0.0040	0.0196	0.0003	0.0029	0.0268	
4	0.05	0.40	0.080	0.040	49	0.0061	0.0393	0.0006	0.0122	0.0521	
Open Hearth Steel													
5	0.08	0.40	0.050	0.030	38	0.0048	0.0341	0.0005	0.0061	0.0455	
Electric steel													
						Ni	Cr						
8	0.19	0.50	0.020	0.012	0.420	10	0.0047	0.0061	0.0002	0.0015	0.0125
9	0.08	0.35	0.010	0.010	0.09	4.34	1.10	13	0.0082	0.0015	0.0007	0.0000	0.0104
12	0.26	0.43	0.068	0.023	0.015	25	0.0053	0.0098	0.0012	0.0041	0.0214
14	0.45	0.38	0.018	0.022	1.27	32	0.0058	0.0167	0.0013	0.0042	0.0280
15	0.98	0.45	0.158	0.075	0.015	70	0.0043	0.0688	0.0010	0.0083	0.0824
18	0.10	0.35	0.009	0.008	0.17	3.62	0.90	94	0.0018	0.0569	0.0047	0.0012	0.0646
20	0.33	0.38	0.026	0.016	0.10	3.06	1.94	105	0.0109	0.0708	0.0039	0.0056	0.0912
Crucible Steel													
						Ni	W						
21	0.38	0.26	0.050	0.021	0.19	0.65 Cr	29	0.0090	0.0248	0.0004	0.0024	0.0366
23	0.16	0.44	0.008	0.008	0.29	4.0	0.91	50	0.0032	0.0271	0.0022	0.0053	0.0378
26	0.27	0.45	0.010	0.012	0.24	4.0	1.30	152	0.0096	0.1290	0.0041	0.0082	0.1509

Carbon Dioxide.—The amount of CO₂ gas was shown to be uniformly low but the results were somewhat dependent upon

the manner of making the determination and are therefore open to some error.

Carbon Monoxide.—The amount of CO varied within wide limits and it was stated that high CO is a proof that the material was not completely deoxidized. No. 9 was a very carefully worked heat of special steel and showed a very small amount of CO. Comparison of No. 18 and No. 9 as to silicon shows that it does not necessarily follow, from the presence of a large amount of silicon, that the steel is degasified, although we know that the gas present would not be given off during solidification. Even in crucible steel, the absorption of silicon from the crucible walls does not necessarily eliminate the gas.

Hydrogen.—Well made steel contains but little hydrogen, although the amount in the finished product depends to a large extent on the manner in which the heat is finished.

Nitrogen.—Nitrogen was taken as the difference between the other gases and 100 per cent. and therefore the error in its determination contained all of the errors in the other determinations.

Just recently Alleman and Darlington have considered the subject of gases in steel and have given a very thorough review of the literature.¹ They have pointed out in particular the necessity of fusing the sample and, for this purpose, constructed a vacuum furnace capable of working continuously at 1900°C.²

In all of the work so far published no allowance seems to have been made for the presence of oxygen (probably as FeO) and the possibility of reactions taking place during the extraction of the gases. Such reactions undoubtedly occur and when they do, they must affect the determinations. For example, iron oxide and carbon would react and produce an unduly large amount of carbon monoxide while, in the Ledebur determinations, hydrogen and carbon monoxide would react to produce an excessive amount of water. In the usual run this amount of water would be charged against ferrous oxide. In view of these possibilities, and of the use of the determinations, it would seem to be only

¹ *Journ. Franklin Inst.*, 1918, Vol. 185, p. 161.

² Another method of freeing the gases from steel was tried by GOUTAL. In this method the sample was dissolved in a solution of copper-potassium chloride and the gases collected, but it seems probable that an error, due to the reaction between the metal and the solution, must have been introduced. See Seventh Intern. Cong. App. Chem., 1909.

logical, in the analysis of the steel, to include a determination of iron oxide with the gas analyses. In the past these determinations have been isolated with the result that the accuracy of the determinations and the use which might be made of the result, have been seriously impaired. The results of the Bureau of Standards will be awaited with the greatest interest because, at this laboratory, accurate methods are being devised for analyzing the samples for the various gases and the active oxygen *i.e.*, ferrous oxide as compared to manganese oxide and silicate.

Effect of Third Metals on the Gases in Steel.—Donaldson concluded that "the volume of gas dissolved in alloy steels diminishes, according as the special element is nickel, silicon, chromium, or manganese," in the order named and that "silicon and manganese decrease the amount of carbon dioxide present while increasing the amount of hydrogen."¹ It can not be said that the work of Goerens and Paquet verifies these conclusions, especially as regards the effect of silicon. Donaldson's work again verified the findings of other experimenters regarding the effect of temperature on the evolution of gas.

As a matter of fact the equilibria are so little understood that we can not state positively exactly what action silicon (or other element) has on the gases in the steel or on those coming off while the addition is made. Silicon, and other degasifiers, inhibit the gas evolution, but whether on doing so the gases form stable compounds which decompose during the analysis, or whether the gas evolution is merely interrupted by some physical action, to proceed further when the steel is heated in *vacuo*, is not known.

The Effect of Nitrogen on the Properties of Steel.—It is generally conceded, and is probably well proved, that nitrogen makes steel brittle. The amount required to accomplish this in any particular case can not now be determined so that it would be difficult to place a maximum nitrogen content in steel specifications; furthermore, we have no definite means of controlling or limiting the nitrogen in steel during manufacture so that a nitrogen specification does not seem advisable.

Experiments on a graded series of steels containing increasing amounts of nitrogen have led to the conclusion that nitrogen unites with iron to form iron nitride which is extremely brittle

¹ Carn. Sch. *Mem.*, Iron and Steel Inst., 1916, Vol. 7, p. 41.

and which, as it increases in amount, tends to make steel more and more brittle.¹

Commercial steels vary considerably in their nitrogen content. Bessemer steels naturally contain larger amounts than open hearth steel. Strauss reports that at the Krupp plant acid and basic Bessemer steels contain from 0.012 to 0.03 per cent. N and open hearth steel from 0.001 to 0.008 per cent. while Chiyevskii gives 0.015 per cent., as the nitrogen content of Bessemer steel, and of open hearth steel, 0.003 per cent. Grabe reports the nitrogen content of various grades of iron and steel to lie between 0.002 per cent. and 0.0125 per cent., although crucible steel contains somewhat larger amounts.² These small amounts of nitrogen are held to be without harmful influence on the quality of the steel.

In 1907, Stromeier described an effect in mild steel, a mysterious deterioration which he called "aging."³ In 1909, he again considered this phenomenon⁴ and maintained that the cause of this peculiar brittleness was to be found in the presence of excessive amounts of nitrogen. As a result of his investigations he advanced a formula by which to calculate the tensile strength of steel, as follows. $T. S. \text{ (in tons)} = 17.20 + 35 C + 10 Si + 25 (Mn - 1.72 S) + 30 P + 300 N$. In this way nitrogen assists very materially in increasing the tensile strength of steel but its presence also may lead to premature failure on account of its

¹ CHIYEVSKII (*Rev. de Met.*, 1914, Vol. 11, p. 618) examined steels containing from 0.0039 per cent. to 0.22 per cent. nitrogen. STRAUSS (*Iron Age*, 1916, Vol. 97, p. 432) found that the elastic limit and tensile strength are increased and the elongation and reduction of area decreased by nitrogen. TSCHISCHEWSKI (*Engineering*, 1916, Vol. 101, p. 171) showed that nitrogen increases the hardness and lowers the elongation and that the effect of nitrogen is particularly apparent in cast steel after quenching and tempering. BRAUNNE (*Stahl u. Eisen*, 1906, Vol. 26, p. 1357) reported that nitrogen increases the tensile strength and elastic limit and lowers the reduction of area and elongation. The increase in strength reached a maximum at 0.03 per cent. nitrogen and the elongation dropped sharply to 2 per cent. at 0.04 per cent. N, which probably accounts for the decrease in tensile strength above 0.03 per cent. nitrogen. Steels containing above 0.06 per cent. nitrogen were found to be very brittle especially at high temperatures and to break with a so-called "crystalline fracture." This paper was severely criticized, BRINELL remarking that its publication should not have been permitted.

² *Rev. de Met.*, 1908, Vol. 5, p. 353.

³ *Journ. Iron and Steel Inst.*, 1907, No. 1, p. 200 and No. 3, p. 86.

⁴ *Ibid.*, 1909, No. 1, p. 404.

peculiar ageing effect. He gave as the limit of the phosphorus and nitrogen which should be allowed in steel, $P + 5 N < 0.08$ per cent.,¹ and cited steels containing 0.047 per cent. phosphorus and 0.0123 per cent. nitrogen, and 0.052 per cent. phosphorus and 0.020 per cent. nitrogen which were defective. Herwig² adopted the view of Stromeier and ascribed the failure of certain steel rails to the presence of 0.03 to 0.04 per cent. nitrogen. Waterhouse, on the other hand, held that the conclusions of Stromeier were not conclusive and maintained that nitrogen alone was not the cause of the defect described.

In steel works practice, nitrogen enters the steel from the air and the furnace gases. Its absorption may possibly be assisted by the presence of hydrogen from decomposed water vapor, inasmuch as in laboratory practice it has been found by various experimenters that it is necessary to have hydrogen present either as a simple mixture of hydrogen and nitrogen or as ammonia gas in order to cause iron to absorb nitrogen readily.

The presence of commercial amounts of nitrogen has no measurable effect on the critical points of iron and steel, but Andrews found that 0.3 per cent. nitrogen suppresses the critical points of pure iron and the A_{r1} point of 0.6 per cent. carbon steel. This effect was not produced by other gases such as hydrogen, carbon monoxide, and carbon dioxide.

Steels which have been treated with nitrogen so as to form a surface layer containing the nitride are known to be highly resistant to atmospheric corrosion. The surface takes a high polish and the use of such material as mirrors in astronomical instruments has been suggested.³

The opinion is generally held that nitrogen can be partially removed from steel by means of titanium which forms a compound with nitrogen and removes it to the slag. The necessity for such treatment seems to be particularly urgent in the autogeneous welding of steel because here the brittle crystals of iron nitride, which form, make the joint brittle. A dissenting opinion to this statement is that of Chiyeveskii and Blinov who report that the compound of nitrogen and titanium (and of vanadium) is soluble in iron. To support their contention, they cite a case of Bessemer steel, which, when treated with ferrovanadium,

¹ *Met. and Chem. Eng.*, 1910, Vol. 8, p. 359.

² *Stahl u. Eisen*, 1913, Vol. 33, p. 1722.

³ F. HANAMANN, Diss. Kgl. Tech. Hochsch., Charlottenburg, 1913.

increased in nitrogen from 0.0105 per cent. to 0.063 per cent.¹

The Effect of Hydrogen on the Properties of Steel.—From the brittleness of electrolytically deposited iron, it is apparent that hydrogen has an embrittling effect on iron and steel, but no definite study has been made on the effect of hydrogen in increasing amounts on the properties of iron and steel.

It is evident from what has been stated that other things being equal, the better grades of steel contain smaller amounts of gases and this is the consensus of opinion. One of the reasons cited for the superiority of well made crucible and electric steel, particularly the former, is that they are both made under conditions which lead to the exclusion rather than the adsorption of gases. This contention finds experimental support in the work of Baraduc-Muller who compared the properties of Bessemer steel both as ordinarily made and after evacuation in a pressure of about 0.5 mm. Hg. His results showed that the treated steel is somewhat stronger and tougher (notched bar test) than the ordinary steel.²

Oxygen in Steel.—It is well known that commercial steel contains slag, silicates and oxides (to be discussed later) so that an analysis capable of bringing out the total oxygen would show considerable of the element to be present. Such a determination can be readily made, as hydrogen is capable of reducing these oxides at 2500°C.³ and the amount of water produced would be a measure of the amount of oxygen present in the steel. Except for giving a rough estimate of the amount of the foreign matter present, such a determination has little metallographical interest, and for two reasons. The determinations are bound to vary with the metallurgical practice in making the steel because sometimes the conditions will be such that considerable slag will be mechanically entrained, while at other times the opposite conditions will prevail. The oxygen determinations likewise will vary, but in an irregular manner, because different oxides will have different oxygen contents and there is no way of telling just which oxides were the source of oxygen during the analysis. Fur-

¹ *Rev. Soc. Russe. Metall.*, 1914, p. 636, through *Journ. Soc. Chem. Ind.*, 1916, Vol. 35, p. 893.

² *Iron and Steel Inst., Carn. Sch. Mem.*, 1914, Vol. 6, p. 216.

³ WALKER and PATRICK, *Cong. for App. Chem.*, Washington, D. C., 1912, Vol. 21, p. 139.

thermore, the oxides which happen to be determined in this way are of importance, not as oxides or as carriers of oxygen, but as foreign inclusions. Consequently the determination of the "total oxygen" in steel is the wrong method of attack and need not be further considered.

Interest in oxygen in steel arose with the introduction of the Bessemer process as it was found that the blown (but not treated) metal was hot short. The addition of manganese eliminated the difficulty and this suggested that manganese converted the oxygen from ferrous oxide, the harmful form, to manganese oxide, a harmless form. Silicon was found to have a similar effect as



×100

FIG. 96.—Oxide spots in failed steel armature shaft.

manganese when it came as a residual of the original silicon of the pig iron and such steel rolled properly. On the other hand, when silicon was added to an overblown heat, a reaction with the ferrous oxide present took place, but the steel remained hot short, somewhat the same as the untreated steel. Investigations as to the amount of this oxygen present and the manner of its combination were instigated and some very interesting, if not entirely reliable, results have been obtained. The appearance of a piece of steel which contains "oxide spots" is shown in Fig. 96. This particular specimen came from a generator-armature shaft of a direct connected turbo-generator used in railway service. The failure was traced to the fatigue-notch effect as this structure lacks adequate resistance.

Ledebur devised the method of treating a sample of the steel with hydrogen at a low red heat, weighing the amount of water which formed supposedly from ferrous oxide and calculating the oxygen to FeO . This method has since been used by a number of experimenters who have determined the oxygen content of various kinds of steel, and it is now being systematically investigated by the Bureau of Standards. The principal difficulties which have been encountered are in interpreting the determination and in devising experimental means for carrying out the analyses.¹ The recent work at the Bureau of Standards has brought out certain defects in the usual Ledebur determinations, principally the reduction of some of the carbon monoxide which is invariably present. This work has also shown that, aside from these two substances, other oxides which are generally present in steel (manganese oxide, silica, etc.) are not reduced under the conditions of the Ledebur determination so that we may assume that ferrous oxide is the principal source of the oxygen found. Subject to these inaccuracies, we may draw the following tentative conclusions.

Oxygen determined by reduction with hydrogen (called Ledebur oxygen) is present principally as ferrous oxide. This amount of oxygen is always very small, probably under 0.10 per cent. even in highly "oxidized" steel. Shimer and Kichline found, for example, that even the most drastic attempts to "oxidize" steel failed to put as much as 0.10 per cent. oxygen in it. Finished steel, that is steel which has been treated with ferromanganese, etc., contains under 0.023 per cent. oxygen according to Shimer and Kichline, and generally under 0.020 per cent. according to Pickard and Potter, although the latter authors state that it is possible to make all grades of steel with less than 0.010 per cent. oxygen, as determined according to their method, being understood. The Ledebur oxygen found by Schmitz in various

¹ Bibliography. BAKER, *Carn. Sch. Mem.*, Iron and Steel Inst., 1909, Vol. 1, p. 212. CUSHMAN, *Journ. Ind. and Eng. Chem.*, 1911, Vol. 3, p. 372. PICKARD, *Carn. Sch. Mem.*, Iron and Steel Inst., 1913, Vol. 5, p. 70. SHIMER and KICHLINE, *Trans. A. I. M. E.*, 1913, Vol. 47, p. 436. PICKARD and POTTER, *Journ. Iron and Steel Inst.*, 1914, No. 2, p. 181. PICKARD, *Carn. Sch. Mem.*, Iron and Steel Inst., 1916, Vol. 7, p. 68. OBERHOFFER, *Stahl u. Eisen*, 1918, Vol. 38. SCHMITZ, *Stahl u. Eisen*, 1918, Vol. 38, p. 541. CAIN and PETTIJOHN, Bureau of Standards, *Tech. Paper*, No. 118, 1919. *Technical Paper*, No. 126, 1919; *Scientific Paper*, No. 346, 1919; CAIN and ADLER, *Scientific Paper*, No. 350, 1919.

grades of steel and ferro-alloys is as follows: wrought iron, 0.217–0.244 per cent.; ingot iron 0.031 per cent.; crucible steel (1 per cent. carbon), 0.24 per cent.; nickel steel (25 per cent. nickel) 0.020 per cent.; high speed steel, 0.024 per cent.; gray cast iron, 0.001–0.005 per cent.; Swedish white iron, 0.002 per cent.; spiegel, 0.008–0.110 per cent.; silicospiegel, 0.037 per cent.; and ferro-tungsten, 0.058 per cent.

The answer to the question as to whether “deoxidation” actually lowers the oxygen content will have to await perfected methods of analyzing for oxygen. As for the total oxygen content it seems safe to assume that it can be lowered only in case it is converted into a gaseous product and escapes into the air, or into a slag-forming constituent and escapes to the slag. So the important point here will be to determine whether the ferro-manganese converts the oxygen from a harmful form, such as ferrous oxide into a less harmful or inert form, such as manganese oxide. Pickard (second paper, p. 69) cited one case in which the Ledebur oxygen of a basic Bessemer steel was lowered from 0.077 per cent. to 0.031 per cent. by deoxidation. Shimer and Kichline reported a drop in oxygen when hot metal was added to an over-oxidized bath, and their determinations of oxygen in finished steel showed it to be uniformly lower than in the over-oxidized steel. The most direct evidence on this point is that of Oberhoffer who found in every case investigated that the Ledebur oxygen falls as the manganese and carbon increase during deoxidation. This can not be entirely explained as due to partial reduction of carbon monoxide by hydrogen as that would be liable to lead to the reverse conclusion, so that we are now reasonably certain that deoxidation converts oxygen from an active form, in which it reacts with carbon and produces “effervescence” and blow holes to an inactive form, in which it is more or less harmless. Schmitz likewise found that the oxygen content of basic open hearth steel dropped from 0.066 to 0.112 per cent. before treatment, to 0.014 per cent. to 0.040 per cent. after treatment.

Oxygen in Wrought Iron.—Pickard (second paper) reports that the Ledebur oxygen content of wrought iron is comparatively high, running as high as 0.603 per cent. in one sample. Cushman reports one sample of wrought iron with as much as 0.855 per cent. oxygen. This oxygen does practically no harm in the iron because, as we shall see, it occurs as a highly oxidized slag and

therefore behaves as so much slag and not as iron oxide usually does. The iron oxide of the slag is readily reduced by hydrogen, the same as uncombined iron oxide (Oberhoffer, Matwieff).

Before leaving this subject it should be noted that no one has as yet pointed out the difference between iron oxide in wrought iron, a relatively harmless constituent, and iron oxide in steel, a relatively harmful constituent.

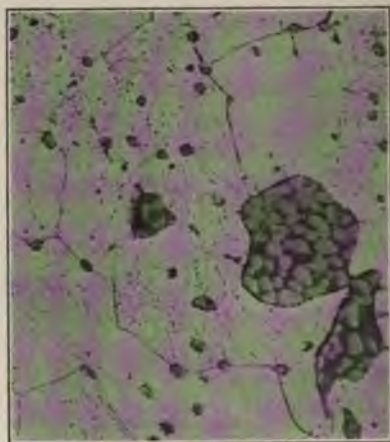
Foreign Inclusions in Wrought Iron and Steel.—If commercial steel were to be given a more rigid definition, according to what has been said, it would have to be considered as an alloy of iron, carbon, manganese, phosphorus, and (at times) silicon. This is because all of these elements, and not alone iron and carbon, have an important influence on the properties of the finished product. That this is so is commonly recognized in the customary specifications and chemical analyses which are written to include these elements. To these must now be added the so-called "foreign inclusions" which always are to be found in commercial steel. As yet, however, and in spite of the fact that they are known to affect the quality of the product, foreign inclusions are not commonly determined and are not commonly included in specifications. It is true that rejections are frequently based on the presence of too much foreign matter, found either in the test bars or in the part under inspection, but these cases are somewhat special.

Foreign inclusions can be divided conveniently, and in strict accordance with their origin, into furnace slag, products of bath reactions, and included extraneous matter.

Furnace Slag.—Steel and wrought iron, as ordinarily made, always come in intimate contact with the furnace slag and it frequently happens that some of this is mechanically entrained, to occur later in the finished product. In the case of wrought iron, the slag is intimately mixed with solid metal, as compared with steel, which is in the molten state when in contact with the furnace slag, so that comparatively larger amounts of foreign matter are found in wrought iron than in steel.

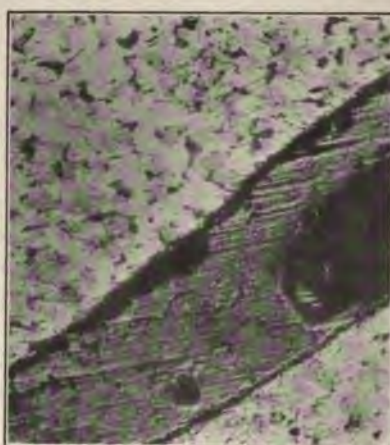
The slag contained in wrought iron is the same material as that which is squeezed out during rolling, which is known to contain mostly iron oxide with some silica and manganese oxide and at times phosphorus. The structure of this slag is shown in Figs. 16 and 97. These photographs show that the inclusions are at times simple and at times binary. In the latter case the

light constituent frequently occurs as primary dendrites and the dark as a fine grained eutectic. The exact identity of the constituents is not known but it seems highly probable that the simple constituent and the dendritic constituent are some solid



X500

FIG. 97.—Slag in wrought iron. (Hancmann.)



X200

FIG. 98.—Furnace slag in steel.

solution of Fe_2O_3 and FeO ; *i.e.*, one of the series described by Sosman and Hostetter.¹ The other constituent, found only

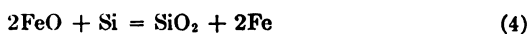
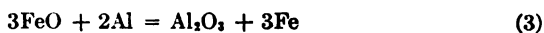
¹ *Journ. Amer. Chem. Soc.*, 1916, Vol. 38, p. 807.

e eutectic, is probably a silicate of iron. Until the equilibrium relations between FeO , Fe_2O_3 and SiO_2 , in the presence of iron, is known it will be difficult to identify these phases.

From the practical point of view the exact constitution of this slag seems to be of minor consequence, greater importance being placed on the amount present, its form and distribution.

The furnace slag contained in steel occurs as rather large irregularly shaped stringers which are elongated in the direction of the work. Such an inclusion is shown in Fig. 98. The composition of such a stringer is probably essentially the same as that of the furnace slag although it is entirely possible that it might have been affected somewhat by changes going on within the bath.

Products of Bath Reactions.—The possible products which might form as the result of bath reactions during the refining and pouring of a heat of steel are considerable in number. The ones whose identity is known with greatest certainty are those which result from the reactions between manganese and iron sulfide, and between aluminum or silicon and iron oxide. These reactions, along with the reaction between manganese and iron oxide, may be written



If these simple reaction products it seems evident that MnS , Fe_2O_3 and SiO_2 form readily while evidence that MnO occurs as a separate and distinct foreign inclusion is lacking. The appearance of certain of these constituents under the microscope is shown in the following photographs. MnO when mixed with steel chips, placed in a hole drilled in a steel block and the block forged at a high temperature, has an appearance similar to MnS .

From the fact that these reaction products form, it is probable that the simple reactions, at least 1, 3, and 4, take place. In textbooks on metallurgy, reaction No. 2 is assumed to illustrate the deoxidation of steel by ferromanganese, and on this account is quite noteworthy that MnO as a foreign inclusion has never been identified. Its appearance is very similar to that of

manganese sulphide and it is possible that many times constituents which are called manganese sulphide are in reality the oxide. But for the present this question must remain open, or until positive methods of identifying manganese oxide have been worked out.

In the case of partial or incomplete reduction of the oxide, we may have an iron oxide, the appearance of which is similar to that of manganese sulphide. The occurrence of this oxide and a method of etching to distinguish it from manganese sulphide have been discussed by Comstock. He found that hot sodium picrate dissolves the sulphide but has no effect on the oxide, a simpler and more reliable method than that of Liesching. The

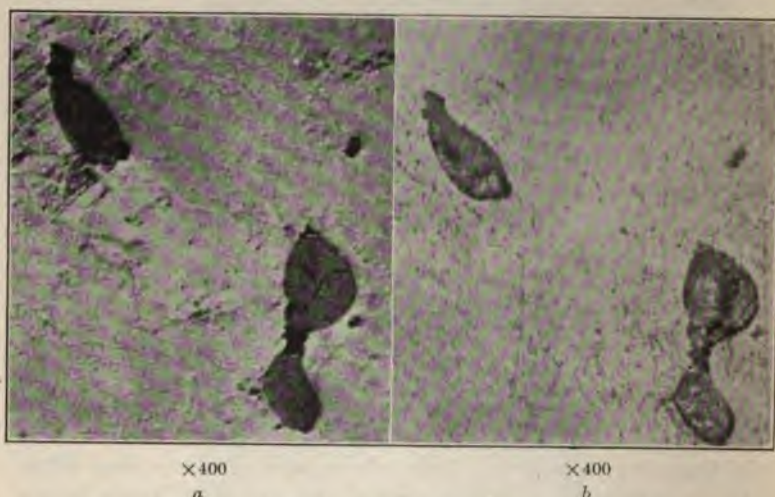


FIG 99.—Manganese sulphide in steel. (a) unetched; (b) etched with hot sodium picrate. The inclusions are dissolved by the treatment.

solvent action of hot sodium picrate is made clear by Fig. 99 which shows stringers of manganese sulphide before and after etching.

It is also possible to have modifications of these reactions due to the solubility or chemical union of the various sulphides and oxides present; thus, MnS is supposed to dissolve considerable amounts of FeS , so that the constituent which is commonly identified as MnS , frequently contains FeS in solution. Similarly SiO_2 which is formed as a reaction product may at times unite with FeO or MnO or with both to form silicates. A silicate

which is supposed to have formed in this manner is shown in Fig. 100 although it will be difficult to state positively that the inclusion is not merely entrained furnace slag.

Extraneous Matter.—The molten steel is always in contact with refractory material such as ladle lining, runner brick, etc. and it is known that considerable amounts of these materials enter the steel. An example of this action is to be had in an investigation at one of our steel plants which was conducted by the writer. This investigation showed that over 1,000 pounds



×400

FIG. 100.—Silicate slag in steel. This inclusion is not dissolved by sodium picrate.

of ladle lining was taken up by each 100 ton heat of steel poured. The analysis of the loam used for lining material was: SiO_2 = 61.96 per cent.; Al_2O_3 = 17.13 per cent.; Fe_2O_3 = 4.95 per cent.; CaO = 3.36 per cent.; MgO = 2.67 per cent.; loss on ignition = 8.41 per cent. Most of this undoubtedly works its way up into the slag. An indication of this action is to be had in the marked increase in SiO_2 and drop in CaO contents of the ladle slag, as compared to the furnace slag, which frequently occurs. The inclusion of this material in steel and its interaction with manganese have been described by McCance.¹ The principal difference in composition between these inclusions and furnace slag or synthetic slag (reaction products) is their high alumina content.

¹ *Journ. Iron and Steel Inst.*, 1918, No. 1, p. 239.

Effect of Foreign Inclusions.—For our present purposes, foreign inclusions in steel can be conveniently classified as those which are plastic at the normal forging temperature and those which are not. Among those which are plastic are manganese sulphide, at least one oxide of iron, the silicates, furnace slag, and a considerable portion of the included extraneous matter. The particles are drawn out into elongated stringers during the rolling or forging and do no material harm, at least during rolling. Neither is the steel materially injured by their presence when it is subsequently stressed in the direction parallel to the long axes of the inclusions. It is when the material is stressed transversely that the harm caused by these foreign inclusions becomes apparent. A number of cases will serve to make this clear.

In Table 70 are given the results of Professor Arnold, reported by McWilliams and Barnes, on test bars taken parallel to and perpendicular to the foreign inclusions.¹ The moderate lowering of the reduction of area in the transverse sections indicates that the number of foreign inclusions is not excessive, although the "toughness," as determined by Professor Arnold's test, is very materially reduced.

TABLE 70.—EFFECT OF FOREIGN INCLUSIONS; LONGITUDINAL VS. TRANSVERSE BARS

Section	Tensile strength, lb. per sq. in.	Elongation, per cent. on 2 in.	R. A., per cent.	Arnold's number
Longitudinal.....	62,720	33.0	55.2	293
Transverse.....	60,928	28.0	47.7	118

Professor Arnold, in discussing McCance's paper, referred to tests carried out on a shaft of a large cruiser which had failed. Longitudinal sections showed an endurance number of 300 ± 20 while the transverse sections showed an endurance number of 250 ± 20 . The fractures of the transverse bars had the appearance of similar fractures of wrought iron except that in the case of the steel the fibre was produced by manganese sulphide.²

¹ *Journ. Iron and Steel Inst.*, 1909, No. 1, p. 380.

² This effect has, in fact, been recognized for some time (see for example, HOUGHTON, *Metallographist*, 1901, Vol. 5, p. 267) although it should be remembered that phosphorus and possibly other constituents, through lack of diffusion, produces longitudinal "fibre" and therefore transverse weakness.

Charpy has shown recently¹ that increasing the amount of work done upon a forging increases the impact number (Charpy test) of longitudinal bars but decreases the impact number of transverse bars. The results are summed up in Table 71.

TABLE 71.—EFFECT OF FOREIGN INCLUSIONS; LONGITUDINAL VS. TRANSVERSE BARS

Coefficient of working	Impact figure, mkg. per sq. cm.			
	Longitudinal tests		Transverse tests	
	1	2	1	2
1.7	6.5	7.1	5.3	5.8
3.2	7.9	8.3	3.9	4.1
6.1	9.9	10.1	3.5	3.5

Dr. Mathews, among others, has pointed out the grave danger of these foreign inclusions by their ability to produce internal "notches."² Dr. McCance³ has stated that 90 per cent. of the failures due to faulty material which he has examined, have been traceable to the presence of foreign inclusions, and considers the subject somewhat from the same point of view as Dr. Mathews.

So pronounced is the effect of these foreign inclusions on the properties (principally transverse) of finished steel that there is a decided trend in metallurgical practice to keep them at a minimum. The ideal condition for steel (not in every case, however) would be to have it free from foreign inclusions, but this is not technically possible any more than it is technically possible to produce steel free from phosphorus or nitrogen. The desire to reduce the amount of the foreign inclusions is reflected in the present tendency towards small sized ingots for the manufacture of forgings which are to be stressed transversely. The advantages of this practice are two-fold. First of all small ingots are less liable to contain an excessive amount of foreign inclusions than large ones are, and secondly the smaller amount of work required by the smaller ingots is less liable to weaken the material transversely. But it must be remembered that the longitudinal

¹ *Journ. Iron and Steel Inst.*, 1918, No. 2.

² Discussion of a paper by the author on "Static, Dynamic and Notch Toughness." *Bull.* No. 146, Amer. Inst. Min. Eng., 1919.

³ *Loc. cit.*

properties are improved by work (wrought iron bars, steel wire, etc.) so that the practice in any case should be decided upon after considering the particular requirements of that case.

Sulphur in Steel.—Inasmuch as sulphur occurs in commercial steel as manganese sulphide (reaction No. 1), it was held appropriate to consider the effects of sulphur at this place. The effect of sulphur, as such, or in the absence of manganese, need be but briefly considered.

Arnold, in a series of papers¹ on "The Forms in Which Sulphur Occurs in Steel," has shown that when manganese is absent, the sulphur occurs as FeS, a constituent which segregates as a network between the grains. According to Ledebur, 0.02 per cent. sulphur in this form is sufficient to cause red shortness, wherein lies the greatest danger from the presence of this element. Little or no effect is caused by this sulphur in the cold state, even if it is present up to 0.1 per cent., but fissures and incipient flaws can be formed during forging or rolling which can lead to premature failure. Ledebur states that this red shortness disappears at white heat by the dissolution of the FeS, which was presumably molten at red heat. Red shortness due to this cause is accentuated by the presence of oxygen.

The bad effects of sulphur in small amounts are reduced to a minimum by the addition of a certain amount of manganese, which forms the much less harmful constituent manganese sulphide.² The amount of manganese required can be seen from the following table as given by Arnold.

From this, it follows that the principal reasons for keeping sulphur low in steel are to prevent an excessive amount of manganese sulphide from forming, and to conserve and increase the efficiency of the manganese. The amount of sulphur allowed varies with the grade of the steel but it is usually held below 0.05 per cent. In structural and bar steel, and many other forms requiring longitudinal strength, greater amounts of sulphide might be tolerated; in fact it is quite conceivable that steel for many purposes is benefited by a certain amount of manganese sulphide, provided only that sufficient work is done on

¹ *Journ. Iron and Steel Inst.*, 1914, No. 1, p. 396; 1915, No. 1, p. 271.

² LE CHATELIER also showed that the addition of manganese to iron containing sulphur breaks up the iron sulphide meshes and forms, presumably, a double sulphide of iron and manganese in the form of globules; *Bull. Soc. d'Encour.*, September, 1902.

TABLE 72.—FORMS OF SULPHUR IN STEEL

Ingot No.	Mn, per cent.	S, per cent.	Remarks
1390	0.05	0.67	Type I
1406	0.09	0.55	Presenting only pale brown meshes of sulphide of iron.
1487	0.05	0.65	
1391	0.96	0.53	Type II
1392	0.52	0.58	Containing sharply segregated and sometimes juxtaposed areas of both pale brown sulphide of iron and dove-grey sulphide of manganese in variable proportions determined by the ratio of sulphur and manganese.
1407	0.77	0.32	
1408	0.41	0.53	
1423	0.69	0.54	
1460	0.86	0.44	
1461	0.74	0.42	
1462	0.69	0.20	
1463	0.75	0.45	
1499	1.11	0.52	
1486	1.01	0.28	Type III
			Containing only dove-grey sulphide of manganese.

the material to produce the proper "fibre." Consequently the question of sulphur is a question of manganese sulphide, the amount and nature of the work done on the steel and the service conditions. These points have not been properly borne in mind in the discussions on sulphur which have taken place from time to time.

According to the early, and now orthodox, view regarding sulphur, it is a dangerous element. On this account metallurgical practice has been directed toward keeping it low. Of recent years we have seen attempts to show that sulphur is not necessarily the harmful element it was originally supposed to be and that, therefore, the specifications are at times unduly rigid. One of the first to advance this idea was Thalner¹ who advocated using an acid hearth for making electric steels, with which practice it is not possible to eliminate sulphur from the charge. It was pointed out in the discussion of this paper that the idea was so revolutionary it would be necessary to advance experimental evidence to support the contention.

A very thorough practical demonstration of the effect of sulphur on many commercial grades of steel has been given by Un-

¹ Intern. Congress of Mining and Metallurgy, DUSSELDORF, 1910.

ger as a partial answer to this criticism.¹ These tests included nails, rivets, chains (welding), sheets, tubes, forgings, sections, axles, rails, and wire cable, and from them Unger drew the conclusion that steel can contain a great deal more sulphur than usually permitted (up to 0.1 per cent.) and still be of good quality. Commercial practice was followed in all cases and the finished material was tested in the usual manner.

Tests on a graded series of low carbon steels containing up to 0.15 per cent. sulphur have been carried out by Hayward² which substantiate what has been said regarding the effect of plastically deformed inclusions on steel.³ As would be expected, the effect of high sulphur was found to be most noticeable in the notched bar test. The author apparently started out to show that high sulphur is not necessarily harmful and it is to be regretted that he did not include tests on transverse bars, particularly on notched bars. Certainly the results reported do little to allay the present fears regarding the presence of this element in steel, although, as has been pointed out, they do show that 0.10 per cent. sulphur and above need not seriously impair the static strength and ductility of steel. In the discussion of this paper, Dr. Unger stated that he had found no greater difference between longitudinal and transverse tests in high-sulphur than in low-sulphur steel plates. This is a statement which is apt to be misleading and certainly requires further elucidation. Manganese sulphide is not the only cause of the difference between longitudinal and transverse tests but it is held to be one of the principal causes, and one would certainly expect to find the difference greater on increasing the amount of manganese sulphide, particularly if the Charpy test is used.

Sulphur is at times intentionally added to low carbon steel to improve its free cutting properties. This it does by producing small chips instead of long turnings. Manganese sulphide or sulphur, is generally held to increase the rate of corrosion of steel.

The inclusions which are not plastic at the ordinary forging

¹ *Iron Age*, 1916, Vol. 97, p. 146; *Blast Furnace and Steel Plant*, July, 1916.

² *Trans. Amer. Inst. Min. Eng.*, 1917, Vol. 56, p. 535.

³ The material used was described as $\frac{3}{4}$ in. round bars and nothing on the amount of work which had been done on them was given; consequently the results of the tests cannot be rigidly interpreted. The photomicrographs published offer little assistance as they are evidently cross sections.

temperature are the refractory oxides such as SiO_2 , Al_2O_3 , etc. The common appearance of these inclusions is shown in Fig. 101. From these photographs it is evident that the little particles themselves remain unaffected by the rolling operation but that they are strung out in groups parallel to the direction of working. Similarly, material which is commonly called "oxide," and which is probably iron oxide, occurs as small black patches as shown in Fig. 96. This constituent in many cases, does not appear to be arranged according to the direction of rolling, as SiO_2 and Al_2O_3 are, the reasons for which are not now known,

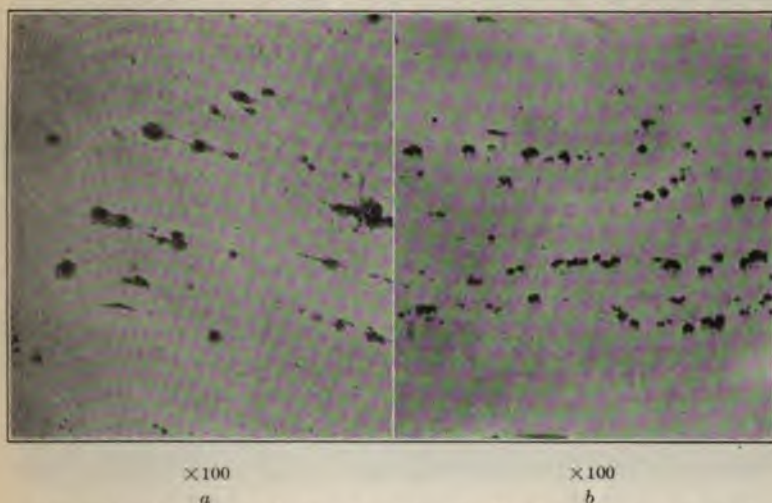


FIG. 101.—(a) Silica inclusions in steel. (b) Alumina inclusions in steel. (Comstock.)

to the writer's knowledge. According to the work of Austin,¹ iron oxide appears to be soluble in γ iron (depression of A_{r_3}) and it might be accounted for on that basis. The relation between this oxide and the oxide described by Comstock, if any exists, is not known.

From the fact that steel, when "wild" in the mold, if treated with an excess of ferrosilicon or aluminum does not roll properly it is commonly held that SiO_2 and Al_2O_3 prevent proper flowage of the metal during rolling and so cause hot shortness. Iron oxide has a similar effect, and hence must be removed by means of manganese.

¹ *Journ. Iron and Steel Inst.*, 1915, No. 2, p. 157.

The danger from these inclusions does not end with the production of hot shortness, as they may be very harmful in the finished product. A good example of this behavior was afforded by a lot of spring steel, examined by the writer, which had the proper chemical composition and had been properly heat treated but failed to show the proper elasticity. The cause was found in the presence of an excessive amount of "oxide." The heat treatment had been unable to overcome the effect of the foreign inclusions. Hibbard has stated that 0.01 per cent. silicon as SiO_2 is sufficient to make steel noticeably red short and to lower the elongation by 10 per cent. of the normal.

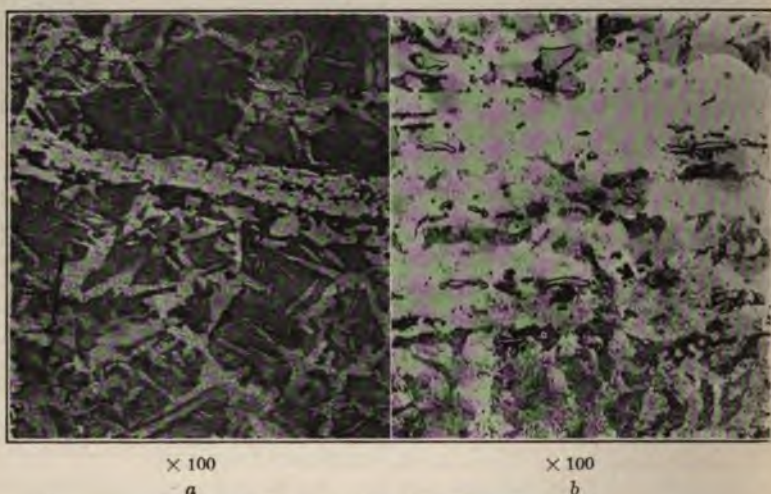


FIG. 102.—Ghost lines in steel.

"Ghosts" in Steel.—A common occurrence in steel is shown in Fig. 102. These markings are referred to as "ghosts" or "ghost lines." The foreign inclusions lying in the central portions of the ferrite segregates are slag, manganese sulphide or oxides. Etching with Rosenhain's reagent shows that the ferrite segregate is also a phosphorus segregate.¹ The possible danger due to the presence of ghost lines may well be imagined inasmuch as we have here a streak of ferrite, known to be weak under certain conditions of strain, whose weakness is reinforced by the presence of an excess of phosphorus and included slag. It is also known that these

¹ The presence of dissolved oxygen in these ferrite bands has also been advanced. (Le Chatelier).

ghosts are not eliminated by the usual processes of heat and mechanical treatment.

There has been considerable speculation as to the cause of ghosts. At first it was held that the foreign inclusions occurring in the bands had acted as an inoculating agent and precipitated the ferrite (Ziegler). It has also been argued that a foreign inclusion also acts as a cavity around the sides of which (*i.e.*, along the crystal borders of the austenite) the ferrite would be segregated. This hypothesis is not without experimental support but it is entirely inadequate to explain the various phenomena associated with ghosts. For example it has been adequately

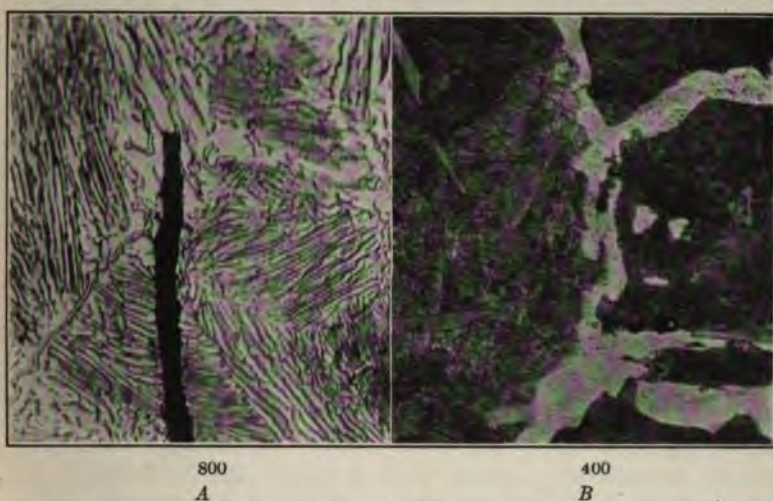


FIG. 103.—Foreign inclusions in steel which have not affected the crystallization.

demonstrated (Stead) that foreign inclusions may occur indiscriminately in ferrite and pearlite. That this is so, is also shown by Fig. 103. At present the occurrence of foreign inclusions in the segregated ferrite is held to be but a coincidence, *i.e.*, that the phosphorus and foreign inclusions both form at the same place but independently of each other, however unfortunate that may be.

The true character of ghost lines is brought out when the structure is developed by heat tinting (Stead) or with an acidulated copper solution (Rosenhain and Haughton). Either of these treatments shows that the segregated ferrite is rich in phosphorus so that a plausible explanation of ghosts must include the effect

of phosphorus. This is further borne out by the fact that an anneal, which equalizes the distribution of phosphorus, eliminates the ghosts (Stead). Such an anneal, unfortunately, is not now commercially economical. We may explain the usual occurrence of ghosts as follows. On cooling through the transformation range, those portions of the steel which are high in phosphorus due to the original segregation during solidification, produce material which contains no carbon. This can be explained on the basis suggested by Dr. Stead by the behavior of phosphorus, which, when it gets an opportunity to do so, expels Fe_3C . So pronounced is this behavior that phosphorus can eject carbon to the dendritic cores, a position which was certainly not occupied by the carbon at the completion of freezing. It also seems possible that phosphorus, by raising A_{r_3} , initiates the ferrite formation along the ghosts which, by coalescence, attracts the ferrite which forms in adjacent areas. In fact, this effect may even account for the ejection of Fe_3C , as the final result will be the same whether ferrite is attracted or Fe_3C ejected. In view of the theoretical importance of the point, it is to be regretted that the effect of phosphorus on A_{r_3} of steel has not been accurately determined.

Quenching from above A_{c_3} is generally sufficient to eliminate the ghost lines but, of course, this treatment has no effect on the phosphorus segregations. Consequently the ghost lines would reappear on slow cooling from above A_{c_3} . It is not always, however, that quenching from above A_{c_3} entirely eliminates ghosts because the carbon, while it would distribute itself uniformly in austenite if given full opportunity to do so, is much slower to "invade" the phosphorus-rich portions than the phosphorus-poor portions and the non-uniform carbon distribution reflects the original ghost lines. The other extreme, *i.e.*, slow cooling, tends to accentuate the formation of ghosts.

A particularly interesting study of banded structure in steel has been made by Oberhoffer and collaborators.¹ Regarding the cause of the ghost lines, it was shown by experiment that forged steel free from phosphorus and slag did not show ghost lines, but that similar steel containing an excess of either phosphorus or slag (manganese sulphide) did show ghost lines. The effect

¹Reference: OBERHOFFER, *Zeit. anorg. Chem.*, 1913, Vol. 81, p. 156 or *Stahl u. Eisen*, 1913, Vol. 33, p. 1569; OBERHOFFER and MEYER, *Stahl u. Eisen*, 1914, Vol. 34, p. 1241; OBERHOFFER and HARTMAN, *Ibid.*, p. 1245.

of heat treatment on the formation of ghost lines was brought out by annealing nickel steel at various temperatures. Thus when the steel was annealed at the proper temperature (Ac_3), ghost lines were not brought out but annealing at 25 to 30°C., either above or below this temperature, brought out ghost lines strongly. Again it was shown that forged steel may have a banded structure if it is reheated above the critical range and cooled slowly; on the other hand if the steel is more rapidly cooled the banded structure will disappear. Forgings many times do not show ghost lines on account of the accelerated air-cooling they receive. On annealing the forging, the proper annealing temperature should be selected if it is desired to prevent the formation of ghost lines.

The effect of ghosts on the properties of commercial steel has not been definitely worked out but the fact that they are known to occur to a considerable extent in commercial steel shows that they are not necessarily injurious. Dr. Stead has stated his belief "that if they are not associated with a material amount of slag inclusions, they are not dangerous or liable to lead to the failure of engineering structures."¹ On the other hand, Dr. Rosenhain has pointed out that in extreme cases these markings may indicate weakness.² On the whole, steel in which the phosphorus is uniformly distributed should be regarded as better grade than steel showing ghost lines, although the mere fact that ghost lines are present should not warrant the rejection of the material unless, in any particular case, the material is known to be injured thereby.

The segregation of phosphorus leads to another effect, the consequences of which may be harmful. Phosphorus dendrites, elongated by forging, accentuate fibre in a longitudinal direction and hence, presumably, weaken the material transversely. The transverse fracture produced, when these phosphorus dendrites prevail, has been termed "woody" and it is known that transverse weakness is associated with this type of fracture.³ It is generally held that gun forgings, on this account, should be made of acid steel, rather than basic, inasmuch as the latter is known to "fibre" more readily than the former. A case of phosphorus

¹ *Journ. Iron and Steel Inst.*, 1915, No. 1, p. 167.

² *Ibid.*, p. 185.

³ This subject has been discussed in considerable detail by PORTEVIN and BERNARD who showed that annealing for three days at 850°-900°C. was in-

banding was noted during the investigation of a fragment of a German "big gun" shell which was picked up on the street in Paris immediately after the explosion. This structure is shown in Fig. 104.

There still remains the possibility of other elements producing these effects, or at least of accentuating the effect produced by phosphorus. At present this can be considered but a fruitful field of research, most of which will probably yield negative results. Ghost lines, woody fractures and other similar effects are usually traced to conditions during melting, refining, cast-



×100

FIG. 104.—Banded structure in steel. Etched with Rosenhain's reagent.

ing and forging operations and consequently will be considered from that point of view in Part III.

sufficient to efface the original structure although annealing for six days produced an equiaxial crystallization in place of the fibre. The reagents used were those given by LE CHATELIER (modifications of STEAD'S). Their formulæ follow.

Methyl alcohol.....	100 cc.	
Ethyl alcohol.....		100 cc.
Water.....	18 cc.	10 cc.
HCl-conc. solution.....	2 cc.	2 cc.
CuCl ₂ .2H ₂ O.....	1 gram	1 gram
MgCl ₂ .6H ₂ O.....	4 grams	
Picric acid.....		0.5 grams

See *Rev. de Metallurgie*, 1918, Vol. 15, p. 273.

CAST IRON

We have already discussed the conditions of equilibrium, both stable and metastable, which exist during the solidification of the alloys containing more than 1.7 per cent. carbon. By way of summary it may be said that, whatever the condition of homogeneous equilibrium of the melt, solidification of the hyper-eutectic alloys proceeds by (1) the formation of the iron carbide along the line $B'-D'$ (Fig. 53) followed by (2) the almost immediate breakdown of the carbide into free graphite or "kish,"¹ the liberation of which causes the composition of the melt to shift to the eutectic composition and (3) the solidification of the eutectic at 1130°C. which is generally followed by (4) the breakdown of a certain amount of eutectic carbide into graphite and solid solution. The solidification of the hypo-eutectic alloy differs from this in that the solid solution, austenite, is the first phase to form in the melt, between the lines $A-b-c-E'$ and $A-B'$. Austenite is a stable phase and consequently it does not break down, as the carbide does, but persists in dendritic form. At B' the austenite-cementite eutectic (ledeburite) forms as before and is subject to the same graphitization, with the exception that hyper-eutectic alloys are apt to contain mechanically entrained crystals of graphite to initiate or accelerate the process.²

The further cooling of the now solid iron proceeds according to the constitution diagram. As soon as the temperature drops below $E'-C'$, the austenite, both primary and eutectic, separate out cementite which, in turn, may break down into graphite and austenite, until at S the austenite has the eutectoid composition. At this temperature the eutectoid inversion takes place with the further formation of cementite. Again this cementite may break down, in whole or in part, into graphite and ferrite.³ The final result of these transformations may be either ferrite + graphite

¹ For a discussion of kish and the concentration of the rising particles in the upper portions of the casting subsequent to the formation of the upper crust, see HOWE, *Met. and Chem. Eng.*, 1912, Vol. 10, p. 359.

² It has been assumed that graphite forms always as a decomposition product of the metastable cementite. It should be noted, however, that an assumption that graphite never forms as a primary phase is directly contrary to theory (GUERTLER) and is even open to question as to fact. (JOHNSON, and GOERENS and SALDAU).

³ It has been advanced by MERICA that a ferrite-graphite eutectoid of low carbon content may form and so produce cast iron of low combined carbon, i.e., cast irons in which graphitization is nearly complete.

(gray cast iron) or ferrite + cementite (white cast iron) or ferrite + cementite + graphite (the intermediate cast irons, commonly called gray cast iron when the fracture is gray), the latter mixture corresponding either to steel or to white cast iron, (depending upon the amount of combined carbon), plus graphite.

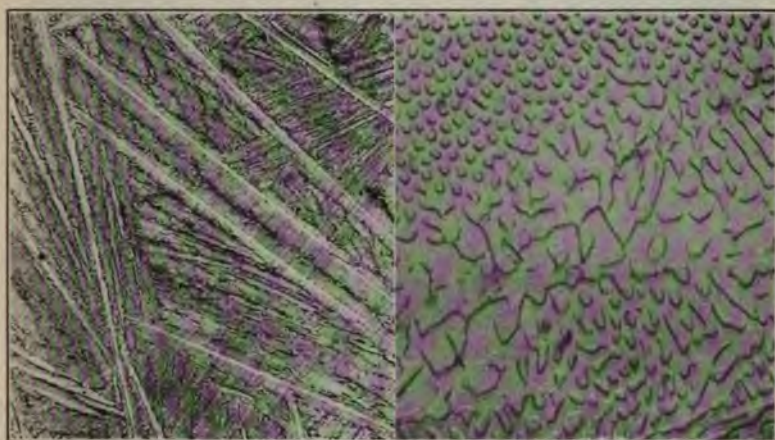
This has been stated by Hatfield as follows: "Carbide is first thrown out of solution which simultaneously dissociates into iron and carbon with the production of kish. The iron then freezes, the eutectic splitting up into austenite (solid solution) and carbide, which latter constituent, controlled by the prevailing conditions of rate of cooling and composition, either persists or dissociates. Further cooling causes the gradual precipitation of further free carbide, which behaves in a similar manner to the carbide separated at the eutectic change point. When we arrive at the temperature of the pearlite change point we still have the solid solution corresponding in composition to hardenite, which now resolves itself into carbide and free iron. The carbide will again either dissociate with the production of perfectly soft pig iron, free from combined carbon or will persist and be recognized as the pearlite in the final iron."

These views are quite generally accepted because it is well known that rapid cooling favors the formation (retention) of cementite and that slow cooling favors the formation of graphite.¹ On the other hand if cementite is reheated, it is known to break down and deposit graphite. These facts indicate that it is the carbide which forms but that graphite is the condition towards which the carbon tends. The extent of the graphite formation depends upon the controlling factors, rate of cooling and chemical composition.

Microstructure of Cast Iron.—The structure of a hyper-eutectic, white cast iron is shown in Fig. 105. The long, unetched, crystal platelets are cementite, Fe_3C . The ground mass is the white iron eutectic, ledeburite, which is shown to better advantage in Fig. 106. Cast iron of this structure has only academic interest because material with this amount of cementite is both exceedingly hard and abnormally brittle. The structure of a

¹ Wüster has shown, for example, that the amount of free carbon increases and the amount of eutectic decreases with the time required for solidification. *Metallurgie*, 1909, Vol. 6, p. 512. See also HEYN and BAUER, *Stahl. u. Eisen*, 1907, Vol. 27, p. 1565.

hypo-eutectic, white cast iron is shown in Fig. 107. The dendritic structure of the austenite, which is now pearlite, and the



×200
FIG. 105.

×1000
FIG. 106.

FIG. 105.—Primary cementite platelets and ledeburite in hyper-eutectic white cast iron. (*E. Leitz.*)

FIG. 106.—Ledeburite. Austenite in cementite. (*Hanemann.*)



×130

FIG. 107.—Austenite dendrite (now pearlite) in hypoeutectic cast iron. (*Hanemann.*)

ledeburite are plainly visible. This photograph represents the structure of white cast iron such as is used to make malleable



FIG. 108.—Gray cast iron. Black patches are graphite flakes.



×1200

FIG. 109.—Quenched cast iron. Constituent in half tone is martensite. (*Hannemann.*)

castings. The structure of cast iron which has been more slowly cooled, in which a considerable portion of the cementite has been converted into flakes of graphite, is shown in Fig. 108. Fig. 109 is added to show that one of the constituents of ledeburite, austenite, forms martensite on rapid quenching. This effect is not as clear in this photograph as it is under the microscope as the structure is very fine and is difficult to reproduce.

Nature of Cast Iron.—There are two conceptions of cast iron which differ from each other quite materially, the first being the one advocated by Howe¹ and the second, the one advocated by Johnson.² According to Dr. Howe's conception, cast iron should be considered as being essentially the same as the particular member of the steel-white cast iron series of the same carbon content as the amount of combined carbon in the cast iron, plus the graphitic carbon. Thus he states³ "the graphite content is of importance not for itself but partly because it is an inverse index of the combined carbon content of the metallic matrix, in the sense that, for given total carbon content, the more graphite there is the less is the content of combined carbon; and partly as a necessary consequence of aiming to have not only a soft, shock-resisting, cheaply machined metallic matrix in the casting itself, the product, but also for the foundry process a material initially cheap, cheaply melted, and readily cast even into intrinsically difficult shapes, qualities which can be had only by means of a great content of total carbon. In some cases, too, the generation of graphite is useful in the process because, occurring as it does during and immediately after solidification, it causes a sudden expansion, which both lessens the tendency of the castings to tear themselves in pieces during solidification, and causes them to reproduce more accurately the shape of the pattern.

"But these are benefits not to the product but to the process. In the product itself graphite is usually only the lesser of two evils. Given a great carbon content for the needs of the process, that carbon not only weakens and embrittles the product less, but hardens it less and thus makes it cheaper to machine, if present as graphite than if present as cementite.

"Thus the justification of my assertion early in this chapter that in the last analysis the source and measure of the most valuable qualities

¹The Metallography of Steel and Cast Iron.

²J. E. JOHNSON, JR., *Met. and Chem. Eng.*, 1916, Vol. 15, p. 530.

³*Loc. cit.*, p. 106.

are the same for the cast-iron products as for steel, the content of combined carbon or cementite."

Certainly the idea that the large carbon content in cast iron is a benefit not to the product but to the process is a happy one.

According to Mr. Johnson's conception, graphite, and in particular the amount and mode of occurrence of the graphite, is the important factor in determining the properties and utility of cast iron. According to this conception, cast iron is good or bad according as the graphite, by occurring as large thin platelets, is able to work considerable injury, or, by occurring in dense compact masses, is able to work lesser harm, and according to the amount of graphite present to work harm in either way.

There can be little doubt that the ultimate properties of cast iron depend on both factors, but, as Johnson points out, the latter may completely mask the former. This latter point finds confirmation in the literature and even in Dr. Howe's Fig. 19A which shows a far more uniform variation between tensile strength and graphite, than between tensile strength and combined carbon taken as the difference between the abscissæ of the plotted points. Even the graphite content can not give a reliable index to the strength and other properties because of variations of the size of the particles and their distribution.

The tremendous influence exerted by graphite becomes at once apparent by noting the great difference in strength between the steel of the same carbon as the combined carbon, and the cast iron. Thus steel with a carbon content of 1 per cent. has a tensile strength of about 120,000 lbs. per sq. in. while cast iron with 1 per cent. combined carbon has a tensile strength of 25,000 to 35,000 lbs. per sq. in. It seems only reasonable to suppose that variations due to differences of combined carbon can be masked by differences in the amount and occurrence of the graphite.

Effects of Various Elements in Cast Iron.—In considering the effects of other elements on cast iron the principal points to be considered are their effect on the amount of carbon converted into the graphitic form and their effect on the nature of the graphite. The effect of these elements on the metallic matrix is generally small and is usually not considered. It is by regulating the amounts of the elements or impurities present that the iron founder secures the properties he desires.

Effect of Carbon.—The effect of carbon, *i.e.*, the amount of total carbon present, seems to have been less extensively studied

and to be now less well understood than the effects of other elements so that only a few of the fairly well recognized generalities will be given here. The total carbon does not vary much from 4 per cent. and seldom goes below 3.5 per cent. The more carbon there is present, the greater liability there is for graphite to separate out and soften the material so that if strength is required, the total carbon should be kept on the low side. Whether or not there is a carbon content above which graphitization is especially pronounced can not be stated, although commercial practice seems to indicate as much (Johnson). The work of Wüst and Kettenbach¹ does not give evidence of such a point. These experimenters came to the conclusion that transverse and tensile strength and hardness decrease as the amount of graphite in-

TABLE 73.—CORRESPONDENCE BETWEEN THE DEGREE OF GRAPHITIZATION AND THE PROPERTIES OF CAST IRON

Name	Matrix				Conglomerate or cast iron					
	C.C.	Hard.	Str.	Duct.	Gr.	Name	Hard.	Str.	Brittl.	Total C
Low C steel.	0.06	Minimum	Moderate	Maximum	3.94	Ultra gray	Minimum	Moderate	Minimum	4
High C steel.	1.0	Moderate	Maximum	Good	3.0	Open gray	Moderate	Maximum	Moderate	4
Ultra high C steel	2.0	Greater	Moderate	Small	2.0	Close gray	Greater	Less	Greater	4
White cast iron	4.0	Maximum	Minimum	None	0.0	White	Maximum	Minimum	Maximum	4

TABLE 74.—PROPER DISTRIBUTION OF CARBON BETWEEN THE STATES OF GRAPHITE AND CEMENTITE, TO GIVE VARIOUS PROPERTIES

Properties sought	Example of use	Distribution of C		Color of iron
		Cementite	Graphite	
Resistance to shock	Machinery	Little	Open gray
Softness, easy machining..	Machinery	Little	Open gray
Sharpness of detail; expansion in solidifying	Ornaments	Much	Open gray
Fluidity (phosphorus).....	Pipes	Moderate	Close gray No. 3
Strength.....	Car-wheel centers	Moderate	Close gray
Imperviousness.....	Hydraulic cylinders, radiators.	Very little	Very close gray
Hardness.....	Tread of car wheels	Much	Nearly white

¹ *Ferrum*, 1913-14, Vol. 11, p. 51.

creases. If the iron is to be hardened by "chilling," the total carbon should be on the high side in order to have sufficient cementite to produce the hardness. Tables 73, 74 and 75 are appended to show the proper distribution of graphite and combined carbon to secure certain desirable properties. These tables are due to Howe.

TABLE 75.—APPROXIMATE PROPORTION OF VARIOUS ELEMENTS IN CAST IRON FOR VARIOUS PURPOSES

Quantitative Control of the Distribution of Carbon between States of Graphite and Cementite,
by Silicon, Sulphur, Manganese, and Phosphorus.

		Silicon
Thick and hence slowly cooling machinery castings		1.50 to 2.25
Thin and hence fast cooling castings, ornamental castings.....		Up to 3 or even 3.4
Radiators, etc., needing density and low graphite		1 to 1.75
Car wheels, in order that carbon may shift easily from graphite to cementite.....		0.50 to 0.80
Castings soft enough for machining.....	S	Not over 0.08
Very thin castings needing great fluidity.....	S	Not over 0.05
In good castings usually.....	Mn	0.40 to 0.70
Chilled car wheels.....	Mn	0.15 to 0.30
Machinery exposed to shock.....	P	Not over 0.50
Gas and water mains, and other castings not exposed to shock but needing fluidity.....	P	Not over 1.60

NOTE: If there is much sulphur or manganese, or if the castings are thin and hence cool rapidly, so that graphitization is restrained, the phosphorus content must be kept lower.

Effect of Silicon.—We have already seen that the amount of graphite in cast iron can be controlled by either physical means—the rate of cooling—or by chemical means, which is done largely by adjusting the amount of silicon. Of these two methods the use of silicon is not only more convenient but leads to a finer and better distributed graphite. In practice both factors must be considered and smaller castings which cool more rapidly contain more silicon than larger castings. One other important effect of silicon is that it lowers the carbon content of the eutectic. This has been worked out quantitatively by Wüst and Peterson whose results are embodied in Fig. 110.¹ At the same time the

¹ *Metallurgie*, 1906, Vol. 3, p. 81.

freezing point of the eutectic is raised to about 1185°C. at 3 per cent. silicon. According to Hague and Turner the eutectic temperature is raised to about 1155°C. at 3 per cent. silicon¹ and the eutectoid temperature to 774°C. The carbon content of the eutectoid was lowered considerably by the addition of silicon, while the temperature of the initial separation of austenite was lowered to 1200°C. at 3 per cent. silicon for a total carbon of 2.77 per cent.²

The silicon present in cast iron is largely dissolved in the matrix but this dissolved silicon does not affect the properties to any

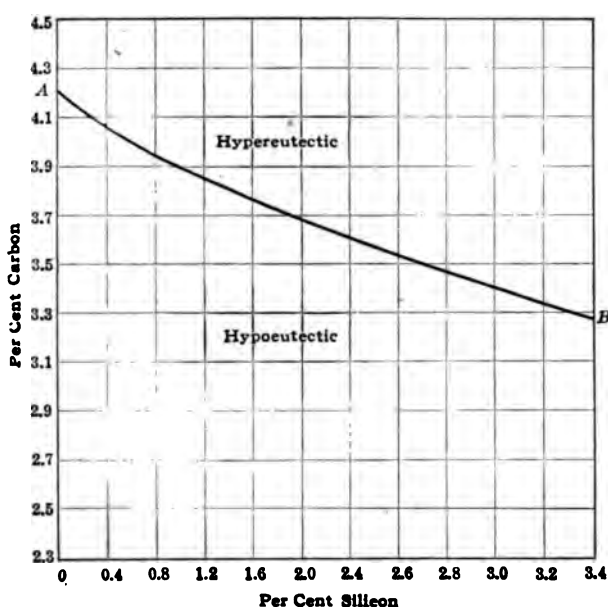


FIG. 110.—Effect of silicon on the carbon content of the eutectic in cast iron. (Wüst.)

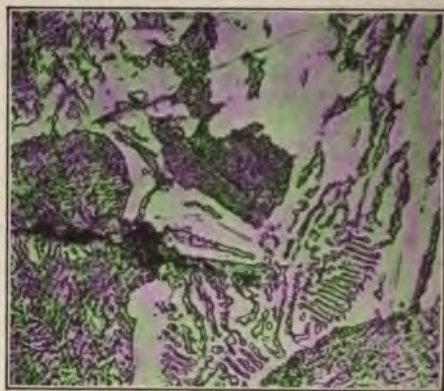
extent. This has been shown by the investigations of Hadfield and Guillet on the effect of silicon on the properties of steel. Therefore the minor effect of silicon on the matrix need not be considered and we shall pass at once to the more important effect of silicon on the properties of cast iron through its behavior in precipitating graphite.

The effect of silicon on cast iron, assuming it to be added in

¹ See also ANDREW, *Carn. Sch. Mem.*, Iron and Steel Inst., 1916, Vol. 7, p. 1.

² *Journ. Iron and Steel Inst.*, 1910, No. 2, p. 72.

increasing amounts, is first to increase the strength and to lower the brittleness by reducing the amount of excess cementite, and then, on further increase, to lower the strength by decreasing the amount of combined carbon or pearlite. The exact effect of silicon, as Johnson points out, depends upon a number of variables so that it is well nigh impossible to discuss it in specific terms. According to the work of Turner¹ who first determined the quantitative effect of silicon, the maximum benefit seems to be derived when the silicon is between 1 and 2 per cent. This range of silicon seems to be fairly well borne out in foundry practice. The amount of silicon required decreases with the size of the casting, with decrease in the rate of cooling and with the



× 800

FIG. 111.—Phosphide eutectic in cast iron—steady state.

pouring temperature and probably varies with other factors such as the amounts of other ingredients present.² Increasing both the carbon and silicon decreases the strength on account of the increased graphite formation (Wüst and Kettenbach, and Stadeler).

The mode of occurrence of silicon in the silicon cast irons is still a matter of conjecture but it seems reasonable to assume that the silicon distributes itself between the austenite and the cementite and that the silicon in the cementite makes that constituent break down more easily at high temperatures (Stead Hatfield). Manganese is supposed to reject silicon from cemen-

¹ *Journ. Chem. Soc.*, 1885, Vol. 47.

² A number of these factors have been considered by HATFIELD, *Journ. Iron and Steel Inst.*, 1906, No. 2, p. 157. See also, HATFIELD, *Cast Iron*.

tite and in this manner, to increase its stability (Hague and Turner).

The following table, due to McWilliam and Longmuir, is added to show the approximate amounts of silicon required for certain particular purposes.

TABLE 76.—SILICON CONTENT OF TYPICAL FOUNDRY MIXTURES

	Per cent. silicon
Chilled gray iron castings.....	0.75 to 1.00
High pressure cylinders.....	1.30
General machinery.....	1.50
Soft iron castings.....	2.50
Stove grate.....	2.50 to 3.00
Hollow ware.....	2.00 to 3.50

*Effect of Phosphorus.*¹—We have already seen that iron and phosphorus form a compound Fe_3P which dissolves in iron up to 1.7 per cent. phosphorus. Fe_3P in excess of 1.7 per cent. forms a eutectic with the solid solution, similar to ledeburite, which is generally known as steadite, in recognition of the work done by Dr. Stead in this field. This eutectic contains 10 per cent. phosphorus and solidifies at 1020°C .²

In cast iron containing both carbon and phosphorus, we have a ternary eutectic composed of the iron solid solution, Fe_3C and Fe_3P . The appearance of the phosphide eutectic in cast iron is shown by Fig. 111. By heat tinting, the phosphide and the carbide can be differentiated. This eutectic has the composition 1.96 per cent. carbon, 6.89 per cent. phosphorus and 91.15 per cent. iron. This was determined by Stead who subjected a Cleveland (phosphoretic) pig iron to hydraulic pressure after practically the whole had solidified. The part squeezed out was analyzed and the corrected composition of the eutectic was found to be about 1.9 per cent. carbon and 6.9 per cent. phosphorus. The effect of phosphorus in lowering the carbon content of the Fe- Fe_3C eutectic is shown in Table 77 taken from Wüst.

¹ For the effect of phosphorus on the iron-carbon alloys, reference is again made to the three papers by STEAD in the *Jour.* of the Iron and Steel Institute.

² KONSTANTINOFF, *Zeit. anorg. Chem.*, 1909, Vol. 46, p. 209. It is assumed here, following DESCH, that the work of SAKLATWALLA (*Journ. Iron and Steel Inst.*, 1908, No. 2, p. 92) is superseded by the more recent work of KONSTANTINOFF.

TABLE 77.—EFFECT OF PHOSPHORUS ON THE CARBON CONTENT OF THE CAST IRON EUTECTIC

Per cent. phosphorus	Per cent. carbon in eutectic
0.02	4.27
0.07	4.22
0.28	4.04
0.88	3.98
2.34	3.34
3.27	3.29
4.61	2.41
5.80	2.25
6.55	2.14

Phosphorus is also known to lower the temperature at which primary austenite first separates, at about the rate of 27°C. for each per cent. of phosphorus.¹ The A_{r1} point was found to come at a constant temperature (710°C.) in cast iron irrespective of the phosphorus content although Desch assumes that the first increment raises the point by a small amount. Phosphorus, in solid solution in iron, lowers the solubility for carbon, and vice versa, so that the decrease in carbon is about 0.3 parts for one part of phosphorus. Stead has concluded that the whole of the phosphorus in highly carburized irons is concentrated in the last portions to solidify.

In commercial cast iron we always have silicon in the presence of phosphorus so that their combined effect must be considered. It has been shown experimentally that, in the presence of silicon, phosphorus assists in the precipitation of graphite although the amount required is quite large. With 0.9 per cent. silicon, at least 3 per cent. phosphorus is required to increase the amount of graphite. With the formation of graphite from cementite, the ternary eutectic disappears and we have in its place graphite and the binary eutectic.² Phosphorus, in the usual amounts, may be said to exert but little influence on the form of the carbon (Stead, Keep). According to Heike small amounts of phosphorus favor the separation of graphite but large amounts prevent it.³

In foundry practice, phosphoretic cast irons are added to the cupola in order to improve the pouring properties of the mixture. This phosphorus, up to about 0.3 to 0.4 per cent.,⁴ increases the

¹ Wüst, *Metallurgie*, 1908, Vol. 5, p. 73.

² Gutowsky, *Metallurgie*, 1908, Vol. 5, p. 463.

³ *Stahl u. Eisen*, 1914, Vol. 34, p. 918.

⁴ Wüst and Storz have shown that the static strength of gray iron is increased by phosphorus up to 0.3 per cent. but that shock tests show that

strength and does not segregate seriously; but if larger amounts are added to secure greater fluidity, the mechanical properties suffer. In exceptional cases over one per cent. is added when pouring extremely thin castings or castings of minute and intricate design. One of the leading manufacturers of automobiles specifies cast iron with 0.35 per cent. phosphorus for engine cylinders, which is cited to show that this element should be kept tolerably low in high grade work.

The Effect of Manganese.—The first effect of manganese in cast iron is to combine with sulphur and form manganese sulphide; both the manganese and sulphur thus combined become neutral. It is the effect of the remaining manganese that will be considered here. The effect of manganese on silicon-free cast iron is free from complications. From the constitution diagram as laid down by Goerens¹ it is seen that the addition of manganese introduces no additional constituent, as the addition of phosphorus does, and its most characteristic behavior is to increase the stability of Fe_3C . The addition of manganese lowers both the temperature of primary solidification² and the eutectic temperature.³ The latter is gradually lowered to 1120°C. by 13 per cent. manganese.⁴ As the manganese content increases above this amount, the solid solubility increases and the alloys resemble more and more the manganese-manganese carbide alloys whose constituents are soluble in all proportions in the solid state (Stadeler). The melting point is gradually raised (above 13 per cent. manganese) to 1260°C. at 80 per cent. manganese. The carbon content of the eutectic is but slightly lowered by manganese and for practical purposes need not be considered (Wüst, Coe). The maximum saturation concentration of carbon in γ iron is not greatly affected although larger amounts (5–10 per cent.) raise it.⁵ The eutectoid temperature is probably not greatly affected by manganese, although, by increasing the hysteresis, the temperature at which the inversion

even smaller amounts are harmful. They also noted the important point that phosphorus causes graphite to collect in pockets. *Ferrum*, 1915, Vol. 12, pp. 89, 105.

¹ *Metallurgie*, 1909, Vol. 6, p. 537.

² Coe, *Journ. Iron and Steel Inst.*, 1910, No. 2, p. 155.

³ Wüst, *Metallurgie*, 1909, Vol. 6, p. 3.

⁴ Coe found that more than 20 per cent. Mn is necessary to lower the eutectic temperature.

⁵ Lutke, *Metallurgie*, 1910, Vol. 7, p. 268.

occurs is materially affected. The results of Wüst are given in Table 78, the points given being the temperatures corresponding to the "peaks" on the heating and cooling curves (inverse rate curves). These figures show that 1 per cent. manganese lowers Ar_1 by 20–25°C.

TABLE 78.—EFFECT OF MANGANESE ON THE PEARLITE POINT IN CAST IRON

Per cent. Mn	Ac_1 , °C.	Ar_1 , °C.	Hysteresis, °C.
1.53	775	675	100
4.90	775	580	195
7.53	not present	not present	

These results are confirmed by Coe, who noted that the pearlite becomes finer and more like sorbite up to 5 per cent. manganese. With more than this amount of manganese, the γ solid solution remains undecomposed down to room temperature (Wüst). This change is accompanied by an increase in hardness up to a maximum at 6 per cent. manganese, which is followed by a decrease above that point (Coe). Under cooling conditions which rendered manganese-free cast iron quite gray, Wüst found that the addition of 1.53 per cent. manganese was sufficient almost completely to suppress the graphite formation.

The effect of manganese on cast iron containing silicon is not as well known, which is due to the complications arising from the effect of silicon in precipitating graphite. Coe has shown that 2.50 per cent. silicon is sufficient to precipitate considerable graphite even in the presence of 16 to 18 per cent. of manganese. Manganese in the ordinary amounts does not seem capable of suppressing the action of silicon to any extent and Coe found more graphite with 2.5 per cent. manganese than with 0.5 per cent. manganese. Manganese was found to have but little effect on the freezing point but Ar_1 was lowered even more rapidly than in the white iron series (Coe). Hatfield confirms this point and reports that the pearlite point disappears abruptly with less than 4 per cent. manganese and assumes this as an explanation of the fact that high manganese produces hard white cast iron. The γ solid solution makes its appearance before graphite disappears, which in itself tends to make the iron white.¹

¹ GUILLET, *Compt. Rend.*, 1908, Vol. 146, p. 74.

The efficacy of manganese in foundry practice is somewhat of a disputed question, in that some favor it to neutralize sulphur, improve the chilling properties, etc., and others keep it low on account of its tendency to produce brittleness and coarse crystallization. Johnson states that manganese "deoxidizes" cast iron and on that account should be kept tolerably low in castings where strength, closeness of grain and chilling power are important. It is true, high manganese can produce these properties but they can be more satisfactorily secured by other means.

It is generally accepted that manganese has a double effect, or that manganese in small amounts affects gray cast iron somewhat differently from manganese in large amounts. The first additions soften the iron and assist the graphitization, while larger amounts produce the well-known hardening and embrittling effect.¹ This shows that manganese should be kept tolerably low—preferably about 0.3 per cent.

Fletcher, in a paper on "The Influence of Gases on the Structure of Cast Iron and Steel,"² remarks that silicon and manganese together aid the escape of gases by keeping a certain portion of the alloy liquid, the silicon being somewhat stronger in its action than manganese. According to Keep, manganese has nothing to do with the grayness of cast iron or with the chill, which are accredited to silicon. He reports that an increase of 1 per cent. of manganese raises the shrinkage by 26 per cent. For a soft iron without shrinkage, manganese should be absent, yet it does not seem that where manganese in pig is below 0.75 per cent. to 1 per cent. its presence will ever be noticed. The small portions of manganese found in commercial foundry irons will have little if any influence on the strength. It is apparently very difficult to determine the effect of manganese on the chill although an increase of 1 per cent. of manganese increases the hardness by 40 per cent. The difference in hardness between the chilled and the non-chilled portions of a casting was found to be less with manganese present than when not, but if a hard chill is required, manganese gives it by adding hardness to the whole casting.

The Effect of Sulphur.—We have seen that the effect of impurities in cast iron, both qualitatively and quantitatively but especially qualitatively, varies with the amount of the impurity

¹ WÜST and MEISSNER, *Ferrum*, 1913-14, Vol. 11, p. 97; OUTERBRIDGE, *Met. and Chem. Eng.*, 1911, Vol. 9, p. 312.

² *Proceed. Staffordshire Iron and Steel Inst.*, 1907-8, Vol. 34, p. 43.

and with the amounts of other impurities present. This is due to the complexity of cast iron and to the interference of one element with the behavior of another. The behavior of sulphur is no exception to this rule and for simplicity we shall consider first the simple effect of sulphur and then its effect in the presence of manganese and silicon.

Sulphur, like manganese, lowers the melting point and eutectic temperature but does not seem to affect the pearlite point,¹ which indicates that sulphur is practically insoluble in γ iron. The sulphur is present largely as FeS which occurs in the eutectic as lines between the grains and as small globules in or between the crystals of iron carbide. Sulphur also undoubtedly occurs in solid solution in the iron carbide up to about 0.1 per cent. sulphur. More than this amount of sulphur crystallizes in the iron carbide as small inclusions and is clearly brought out by heat tinting.² It is known that sulphur tends to produce white cast iron, and in fact in the absence of silicon only a small amount of sulphur keeps all of the carbon in the combined form,³ a fact which is explained by the presence of the sulphur in solution in the carbide.

The chemical explanation of the effect of sulphur in producing white cast iron has been disputed by Levy⁴ who advances the theory that the sulphide in the eutectic and the resultant sulphide films about the particles of Fe_3C prevent the decomposition of the latter and white iron results. This opinion is concurred in by Liesching.

The effect of adding sulphur to cast iron (assuming low manganese and silicon) is to increase the strength and hardness and is regarded as a detriment. In the presence of manganese, the sulphur is converted into the inert form, MnS , which action explains the softening effect of the first additions of manganese.

The effect of sulphur on cast iron in the presence of silicon has been thoroughly investigated by Hatfield⁵ who showed that silicon overcomes the influence of sulphur to retain the carbon in the combined form, about ten parts of silicon being required to offset one part of sulphur (Johnson). As Professor Howe pointed out in the discussion, the important point here is not

¹ LIESCHING, *Metallurgie*, 1910, Vol. 7, p. 565.

² STEAD, British Association for Advancement of Science, 1910.

³ COB, *Proc. Brit. Foundrymen's Assoc.*, 1911-12, p. 78.

⁴ *Metallurgie*, 1908, Vol. 5, p. 327.

⁵ *Journ. Iron and Steel Inst.*, 1913, No. 1, p. 139.

the total amount of silicon and sulphur present, but the amounts present in solution in the carbide.

In foundry practice sulphur is regarded as a very harmful element, a point which has added to the popularity of charcoal iron as compared to coke iron, although, according to Johnson, the real virtue of charcoal iron is to be found in another direction, *i.e.*, oxygen. Aside from its hardening effect, sulphur is held to be harmful on account of its tendency to liquate, and, by producing excessive shrinkage, its tendency to produce cracks in the castings. Sulphur is particularly harmful in chilled car wheels on account of the rapid temperature variations which tend to produce cracks.

The Effect of Oxygen.—Our knowledge regarding the behavior of oxygen in cast iron is due, almost entirely, to the work of J. E. Johnson, Jr.¹ According to Johnson the reason for the superiority of charcoal iron is to be found, not in its low sulphur, but in the large amounts of (unreduced) oxide which it contains. This oxide results from the low temperatures at which this iron is produced. On account of the effect of manganese in reducing this oxide, Johnson recommends that manganese be kept low in the better grade of castings.

The effect of high oxygen (0.3 per cent. \pm , as compared to 0.01 per cent.) may be briefly stated as follows. Oxygen seems to improve the structure of the metallic matrix and to decrease the injury done by the graphite present by causing it to separate out in "nodular" form instead of as large flakes. At the same time oxygen seems to prevent the total decomposition of the carbide so that the matrix generally contains above 0.6 per cent. carbon, while the amount of the harmful constituent (graphite) is correspondingly reduced. This retarding action of oxygen is noted particularly in chilled iron. The chilling effect, as the silicon decreases, is noted earlier in the high oxygen irons than in the low oxygen irons. The embrittling effect of oxygen on the metallic matrix (steel) is not noticed here inasmuch as it is more than offset by the effect of oxygen on the condition of the graphite.

The Effect of Titanium.—The effect of titanium on cast iron has been thoroughly discussed by Bradley Stoughton who gives a thorough review of the literature as well as a report of his own

¹ An account of this work is to be found in *Trans. Amer. Inst. Min. Eng.*, 1915, Vol. 50, p. 344; also in *Met. and Chem. Eng.*, 1916, Vol. 15, p. 590.

investigations.¹ As a result of this work we may conclude the following. In commercial foundry practice the addition of titanium is beneficial, not because it produces new properties in the iron but on account of its effect on the quality. Only small amounts, from a trace up to 0.10 per cent. titanium should remain behind in the iron. In this respect the action seems to be of the same nature as that of phosphorus in bronze. Stoughton points out in particular that these benefits are secured only if the treatment is correctly performed. When this treatment is known and properly carried out the iron is increased in strength, over non-treated iron, by amounts up to 50 per cent. and in toughness and durability to a like degree. When titanium is used in iron for the manufacture of car wheels or rolls, the amounts of silicon and manganese must be varied in accordance, but the chill is said to be harder and the core tougher and stronger. According to Johnson, the titanium treatment would be harmful to high-oxygen iron by reducing its strength and chilling power.

The Effect of Aluminum.—Keep² early determined that the influence of aluminum in cast iron is to make white cast iron gray, and with the addition of 0.75 per cent., to keep the iron from chilling when cast in an iron mold. He also found that aluminum, like silicon, reduces the total carbon. Hogg³ found that, with white Swedish iron, practically the whole of the carbon was set free as graphite by the addition of about 1 per cent. of aluminum. In a systematic investigation, Mellen and Waldron⁴ sought to determine the amount of aluminum necessary to produce the maximum separation of graphite in a white iron which was as free as possible from silicon and other impurities. It was found that aluminum when below 0.23 per cent. effected practically no separation of graphite in chill cast specimens. The addition of more aluminum produced a rapid increase in the precipitation of graphite, the effect reaching a maximum at about 0.53 per cent. The effect of aluminum on the separation of graphite in the slowly cooled specimens was less regular. It was found that in no case was there less than about 0.9 per cent. carbon retained in the combined form showing that aluminum

¹ *Trans. Amer. Inst. Min. Eng.*, 1912, Vol. 44, p. 382.

² *Trans. American Society for Advancement of Science*, 1888; *Journ. Franklin Inst.*, Vol. 126, p. 220. *Trans. Amer. Inst. Min. Eng.*, 1889-90, Vol. 18, p. 102.

³ *Journ. Iron and Steel Inst.*, 1894, No. 2, p. 104.

⁴ *Journ. Iron and Steel Inst.*, 1900, No. 2, p. 244.

is less effective than silicon. Crushing tests showed that the presence of 0.25 per cent. aluminum reduced the resistance to crushing from about 224,000 lbs. per sq. in. to about 94,080 lbs. per sq. in.

Aluminum is not ordinarily added to cast iron except, perhaps, for its cleansing effect. In this respect its behavior would probably be erratic and dependent upon the condition of the iron.

Effect of Nickel.—Guillet¹ found that nickel, similarly to manganese, causes the disappearance of pearlite and the formation of sorbite and troostite, and that, similarly to silicon, it promotes the separation of graphite.

Effect of Chromium.—Goerens and Stadeler² have shown that chromium up to 5 per cent. has an inappreciable effect on the eutectic and eutectoid temperatures in cast iron containing from 4.0 to 4.7 per cent. carbon. The eutectic composition is increased to 4.7 per cent. carbon. With either 1 per cent. or 2 per cent. silicon, 1.5 per cent. chromium is sufficient to keep the carbon entirely in the combined form, showing that it is unfavorable to the formation of graphite. It is generally assumed that chromium forms a double carbide with Fe_3C and thereby increases its stability.

Nickel and chromium are not commonly added to cast iron but it is understood that such a material, called "Adamite" is used for the manufacture of high grade rolls, etc.

Effect of Vanadium.—The use of vanadium in cast iron has been advocated both on account of its cleansing effect and its physical effect in improving the properties of cast iron.³ Vanadium is said to strengthen the ferrite by entering into it in solid solution and also to increase the stability of the iron carbide. The tensile strength of cast iron is said to be increased 50 per cent. by the addition of about 0.2 per cent. vanadium, although Moldenke reports an improvement of about 100 per cent. for gray iron and of about 200 per cent. for white iron by the addition of about 0.25 per cent. vanadium.⁴ This is verified by the work

¹ *Compt. Rend.*, 1907, Vol. 145, p. 552.

² *Metallurgie*, 1907, Vol. 4, p. 18.

³ SMITH, New England Foundrymen's Assoc., May, 1910.

⁴ *Foundry*, 1908, Vol. 32, p. 17. This figure is the amount of Va remaining in the iron and the conditions of the experiment were such that the amount of Va used in cleansing could not be determined.

of Hatfield¹ who showed an increase in hardness from 387 to 430 on the Brinell scale by increasing the vanadium to 0.65 per cent. The scleroscopic hardness remained constant at 48. No difference in structure was noticed due to the vanadium content. The carbide was separated electrolytically and found to contain the greater part of the vanadium, and, further, the silicon content of the carbide was found to be lowered by vanadium. Heat treatment tests showed that the carbide containing vanadium was more stable than vanadium-free carbide.

Vanadium increases the strength of gray iron by 10 to 25 per cent. It causes a more even distribution of the graphite and produces a finer grained and more uniform structure, while it makes chilled iron stronger and tougher.² Vanadium cast iron is especially recommended for engine cylinders, gears, chilled iron rolls, piston rings, cylinder valves, bushings, and castings which must withstand pressure. The usual amount of vanadium added to cast iron is 0.1 to 0.2 per cent. The machining properties, as well as the strength, are improved by the addition of vanadium.³

Strength of Cast Iron.—The properties of cast iron depend upon the condition of the carbon, whether free or combined, the size and shape of the graphite particles, the chemical composition, and the structure. Naturally a function as complex as this can not be truly represented by means of a simple diagram, but we may get an idea of the tendency of the effect which the carbon condition has on the strength of cast iron from Fig. 112 taken from Howe. The total carbon is assumed to remain constant at 4 per cent.

A good idea of the normal strength of commercial cast iron can be had from the specifications of the American Society for Testing Materials. These are, for gray iron castings: light castings, under $\frac{1}{2}$ inch thick, tensile strength at least 18,000 lbs. per sq. in.; medium castings, under 2 inches, tensile strength at least 21,000 lbs. per sq. in.; heavy castings, over 2 inches thick, tensile strength at least 24,000 lbs. per sq. in. The transverse strength, which is very generally used, is measured with the "arbitration bar" which is 15 inches long and $1\frac{1}{4}$ inches in diameter. By pouring a round bar, irregularities due to cooling strains are

¹ *Journ. Iron and Steel Inst.*, 1911, No. 1, p. 318.

² NORRIS, *Met. and Chem. Eng.*, 1911, Vol. 9, p. 361.

³ FITCH, *Foundry*, 1914, Vol. 43, p. 303.

eliminated. This bar is broken on supports 12 inches apart. The breaking strengths for the three grades of castings are not under 2,500 lbs., 2,900 lbs., and 3,300 lbs. for light, medium and heavy castings respectively.

The compressive strength runs very high and is generally from 80,000 lbs. to 150,000 lbs. per square inch. According to Mills, the ultimate compressive strength in structural columns will seldom exceed 30,000 to 40,000 lbs. per sq. in. but smaller specimens will be found to run from 50,000 to 150,000 lbs. per sq. in. The safe working stress is usually assumed to be about 16,000 lbs. per sq. in. for small castings but for structural members

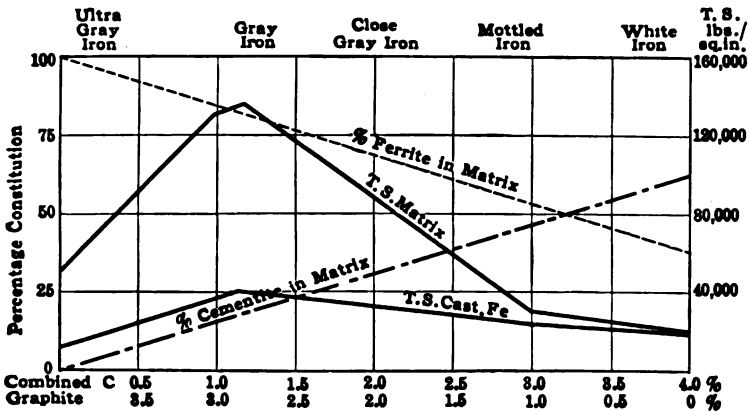


FIG. 112.—Effect of the condition of the carbon on the strength of cast iron. (Howe.)

whose parts are in flexion as well as in compression the safe stress should be reduced to 8,000 lbs. or even less for long columns.

The compressive strength increases with decrease in combined carbon until the eutectic carbon disappears, at which point the maximum strength is obtained. Manganese also materially raises the compressive strength of cast iron.¹

Keep, in a report to the American Society of Mechanical Engineers,² has shown that the compressive strength of cast iron varies with the silicon content and the thickness of the section in the same way as transverse strength and tensile strength. A very valuable report on the microstructure of cast iron is given in this report by Sauveur.

¹ *Com. Journ. Iron and Steel Inst.*, 1910 No. 105.

² *Trans. Amer. Soc. Mech. Eng.*, 190

Adamson gives the following table¹ to show the strength of cast iron of different compositions as produced in ordinary foundry practice.

TABLE 79.—STRENGTH OF COMMERCIAL GRADES OF CAST IRON

Analysis							T. S., lbs. per sq. in.	Trans- verse, 3' 0" centers, cwt.	Deflec- tion inches	Moment of Resist- ance
TC, per cent.	GC, per cent.	CC, per cent.	Si, per cent.	S, per cent.	P, per cent.	Mn, per cent.				
3.56	2.98	0.58	1.53	0.110	1.19	0.90	30,912	34.75	0.336	20.283
3.56	3.03	0.53	1.65	0.098	1.19	0.85	38.5	0.386	20.430
3.57	3.04	0.53	1.67	0.106	1.20	0.85	33,152	36.5	0.329	19.725
3.56	3.00	0.56	1.65	0.075	1.20	0.87	34,496	35.0	0.329	19.523
3.58	2.99	0.59	1.88	0.100	1.17	0.80	33,152	36.5	0.359	20.796
3.57	2.98	0.57	2.00	0.090	1.17	0.81	34,496	30.0	0.314	17.078
3.56	2.98	0.58	1.30	0.077	0.59	0.68	34,944	31.5	0.329	19.125
3.59	3.05	0.54	1.46	0.073	0.84	0.65	32,704	28.5	0.347	17.569
3.56	3.02	0.54	1.72	0.072	0.78	0.66	32,900	29.5	0.350	17.813
3.56	3.00	0.58	1.86	0.072	0.70	0.65	30,600	27.5	0.321	16.588

The diameter of the test bars was $\frac{3}{4}$ inch.

The modulus of elasticity of cast iron has not received the attention which its importance deserves. It is probably true, within commercial limits, that the quality of cast iron can be judged from its breaking strength but it cannot be told from a test to destruction what the exact behavior of cast iron in service will be. This is due to the fact that the modulus of elasticity varies from one casting to the next and also with the stress. Instead of dealing with a constant modulus, as in the case of steel, we are now dealing with a variable modulus. In one case there was a variation of 14 per cent. between two different castings poured from the same ladle.² In another case the modulus dropped from 16,139,700 to 7,849,440 lbs. per sq. in. as the stress increased from 2,275–6,825 to 20,480–25,000 lbs. per sq. in. for a cast iron having a tensile strength of 32,700–34,100 lbs. per sq. in.³ The decrease in the modulus is progressive so that the stress-strain curve is a smooth curve instead of a straight line. There is no proportional limit and no yield point. Cast iron of lower tensile strength has a lower modulus, while quenching increases the modulus and makes it less variable with the stress.⁴

¹ See ADAMSON, *Journ. Iron and Steel Inst.*, 1909, No. 2, p. 208.

² SCHÖTTLER, *Zeit. Ver. deutsch. Ing.*, 1912, Vol. 56, Pt. 1, p. 351.

³ BACH, *Ibid.*, 1900, Vol. 44, Pt. 1, p. 409.

⁴ BACH, *Ver. deutsch. Ing., Mitt. u. Forschungsarb.*, Vol. 1.

On account of the erratic variation of the modulus of elasticity, the true behavior under bending and flexure can not be determined from the usual tests. Schöttler concludes that bending tests of cast iron to destruction are misleading and suggests that the deformations should be determined by some accurate method (Martens mirror extensometer) and stresses calculated from these observations.

Hardness.—The Brinell hardness of various kinds of cast iron is given in Table 80.¹

TABLE 80.—BRINELL HARDNESS OF COMMERCIAL CAST IRON
Diameter of ball, 10 mm.
pressure, 3000 kilos.

	Average hardness number
Glazed iron	143
No. 1 iron.....	104
No. 3 iron.....	112
No. 4 foundry.....	156
No. 4 forge.....	160
Hard forge.....	197
White iron.....	418
Pure Swedish wrought iron.....	87
Hard face of chilled casting.....	445
Middle (mottled) of chilled casting.....	350
Grey back of chilled casting.....	207

Impact Strength.—Cast iron possesses but little impact strength and would naturally not be used for parts which might be subjected to heavy blows. On this account but little work has been done on the impact strength, although more work might be done with advantage, particularly in connection with heat treated cast iron. The relative resistance to impact is usually taken as one-half the product of the breaking load and the total deflection divided by the volume of the specimen between supports in the transverse test. In view of what was said about the variation of the modulus of elasticity, this measurement is open to criticism. At any rate only test bars of the same dimensions should be used for comparison.

It is known that with total carbon under 3.50 per cent. and graphitic carbon under 2.75 per cent. the impact strength increases with the manganese up to about 0.50 per cent. manganese and then falls off gradually with further increase in manganese. With total carbon about 4.0 per cent. and graphitic carbon about 3.25 per cent., manganese has little effect on the impact strength,

¹ STEAD and JONES, *Proc. Cleveland*

Trans., 1906-7.

which is uniformly low.¹ In general, high graphitic carbon and high silicon lower the impact strength while if the transverse strength and transverse bending are high, the impact strength will be comparatively high.² On this account a certain amount of silicon is necessary to produce the graphitization which promotes the transverse bending, but above this amount, the silicon again becomes harmful.

In Table 81 are given some results of Hatfield showing the effect of pouring temperature and heat treatment.³

TABLE 81.—EFFECT OF POURING TEMPERATURE AND HEAT TREATMENT ON CAST IRON

Analysis						Casting temp.	Condition	Max. stress, T per sq. in.	Elong., per cent.	R. A., per cent.
CC, per cent.	Gr, per cent.	Si, per cent.	Mn, per cent.	S, per cent.	P, per cent.					
3.42	0.93	0.10	0.056	0.03	Hot	As cast	11.14		
3.40	0.93	0.10	0.056	0.03	Fair	As cast	7.95		
3.41	0.93	0.10	0.056	0.03	Cold	As cast	17.20		
0.56	2.61	0.93	0.10	0.057	0.03	Hot	H. T.	24.40	1.00	1.50
0.55	2.58	0.93	0.10	0.056	0.03	Fair	H. T.	34.40	1.16	1.47
0.56	2.59	0.93	0.10	0.057	0.03	Cold	H. T.	34.70	2.00	2.70
0.52	2.93	2.14	0.11	0.051	0.04	Hot	As cast	7.01		
0.54	2.94	2.14	0.11	0.053	0.04	Fair	As cast	8.40		
0.54	2.96	2.14	0.11	0.051	0.04	Cold	As cast	12.98		
0.20	3.21	2.14	0.11	0.053	0.04	Hot	H. T.	2.82		
0.21	3.22	2.14	0.11	0.053	0.04	Fair	H. T.	3.20		
0.18	3.17	2.14	0.11	0.052	0.04	Cold	H. T.	3.99		

Test number	C. C. per cent.	Fracture
A1	3.42	White; fairly sharp crystallization.
B2	3.40	White; sharp crystallization.
C3	3.41	White; well mixed crystals.
D1a	0.56	Steely; finely crystallized. Unsound.
E2a	0.55	Steely; finely crystallized.
F3a	0.56	Steely; finely crystallized.
G1	0.52	Gray; crystalline.
H2	0.54	Gray; crystalline.
I3	0.54	Gray; crystallized, but much finer.
J1a	0.20	Dry and gray crystallization.
K2a	0.21	Dry and gray crystallization.
L2a	0.18	Dry and gray crystallization.

H. T. = Exposure of several hours at 900°C. followed by slow cooling over 48 hours.

¹ Wüst and MEISSNER, *Ferrum*, 1913-14, Vol. 11, p. 97.

² Wüst and KETTENBACH, *Ibid.*, p. 51.

³ *Journ. Iron and Steel Inst.*, 1907, No. 2, p. 79. KEEP (*Cast Iron*, 1902) reproduces data showing how various factors influence the properties of cast iron. The data reproduced in tabular form are valuable for reference.

Jüngst¹ gives the results of a large number of mechanical tests on cast iron which bring out the difficulty of getting similar results with cast irons supposedly alike. He points out some of the causes of variations as follows: (1) differences in operation of the blast furnaces; (2) differences in cupola temperatures; (3) differences in the methods of pouring; (4) differences in the rate of cooling of the cast iron. Jüngst remarks that if these four factors are maintained constant in technical practice, the desired regularity in the properties will be satisfactorily met.

Malleable cast iron and "semi-steel" will be considered in Part III.

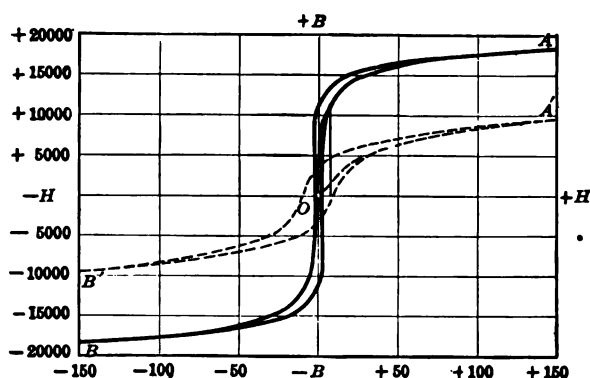


FIG. 113.—Hysteresis curves of pure iron (*A*) and of cast iron (*A'*). (*Gumlich*.)

Magnetic Properties.—Cast iron is used for dynamo frames and other parts of electrical machinery, therefore its magnetic properties are of technical interest. Such castings should be low in carbon and manganese and high in silicon,² although manganese cannot be dispensed with where strength is required.³ The magnetic properties in general are improved by suitable annealing but they deteriorate through rapid cooling.

In white iron, silicon and phosphorus have very little effect on the magnetic properties of very low carbon cast iron, while the influence of manganese is apparently to increase the amount of combined carbon.⁴ The influence of silicon and phosphorus on a low carbon gray iron is indirect and due to their effect on

¹ *Stahl u. Eisen*, 1913, Vol. 33, p. 1425.

² GÜMLICH, *Stahl u. Eisen*, 1913, Vol. 33, p. 2133.

³ GOLTZE, *Giesserei Zeitung*, 1913, Vol. 10, pp. 1, 461.

⁴ SUMMERS, *Journ. Soc. Chemical Industry*, 1897, Vol. 16, p. 998.

the condition of carbon. If it is desired to have high permeability the carbon should be in the free state. The graphite appears to be inert and, if it could be removed without increasing the combined carbon, the permeability would be higher. By the same token, other impurities of high specific volume should be kept low as the active or magnetic volume may be reduced by 20 to 30 per cent.

The curves in Fig. 113, taken from the work of Gumlich, show the comparison between the B-H curves of pure iron and of cast iron.

Permanent Magnets.—The remanent magnetism and coercive force of permanent magnets of cast iron and of good magnet steel have been compared by Campbell.¹ The remanent magnetism of a cast iron magnet was about 1750 while its coercive force was about 51 gauses. The corresponding figures for two magnet steels were 2550 and 2950, and 55.5 and 73.0. Good magnet steel is apparently better for permanent magnets than white cast iron, but the ease with which intricate forms can be cast with the latter material should be considered in the comparison. Gumlich recommends a carbon content of not over 2 per cent., a manganese content of from 1 to 2 per cent. with practically no silicon. Quenching from 800°C. improves the coercive force of permanent magnets as the carbon is most active when dissolved in the iron as martensite. The coercive force of quenched cast iron may run as high as 70, as compared to 8 to 12 for ordinary cast iron or 0.5 to 1 for pure iron.

¹ *Philosophical Magazine*, 1906, November, p. 468.

CHAPTER VI

THE SPECIAL STEELS

We have just seen that the "straight carbon" steels can be produced with a truly remarkable range in physical and mechanical properties and that, on this account, they can be utilized for a great variety of purposes. This range in properties is secured by means of varying the carbon content and of other minor variations in composition, and by heat and mechanical treatment. It is but a truism to state that with no other binary series can such varied or such valuable properties be obtained. Thus we have steels which can be rolled hot into shape or drawn into wire, which can be welded, or stamped or pressed cold, which can be forged into shape and then subsequently benefited by heat treatment, which can be hardened for tools or cutlery or produced with a spring temper, or else cast into shape. It is also noteworthy that the steels possess reasonably good conduction of electricity, high magnetic permeability or high permanent magnetism, which factors in one way or another, materially increase the field of usefulness of these alloys. At no time is the iron content below 98 per cent. so that the cost is never excessive and the materials possess such properties that they are eminently suited for the uses to which they are put.

In the light of the low cost and all around utility of the simple binary alloys of iron and carbon, it might seem as if there were no need of adding other and more expensive ingredients; but experience has shown that by adding elements such as nickel, chromium, etc., the properties and utility can be improved by an amount which is more than sufficient to compensate for the increase in cost. Not only is it entirely possible to produce parts out of special steels which have better properties than they would have if made of carbon steel, but this can be done at a lower cost. In fact these special steels are no longer to be regarded merely as improvements on the carbon steels but rather as absolute requirements in present-day engineering practice. The modern automobile steels, the armor piercing projectile,

ordnance material, and high speed tool steel, offer examples of this point, as we shall see by closer consideration of the special steels involved.

The special steels, like the carbon steels, can be roughly divided into steels used for construction purposes and steels used for cutting purposes. This general classification will be followed here, first for the ternary steels and then for the quaternary or complex steels.

TERNARY CONSTRUCTION STEELS

The ternary construction steels which we shall consider here are those containing nickel, cobalt, copper, manganese, silicon, and aluminum, respectively, as the special constituent.

NICKEL STEEL

The first and also the most important development in the manufacture of steel for construction purposes came with the addition of nickel to the carbon steels. These steels were first described by Riley in a memorable paper before the Iron and Steel Institute read in 1889,¹ although they had been made prior to that time both in France and in England. At that time Riley pointed out the very remarkable, and till that time unknown, combination of high elastic limit and elongation of these steels, although the even more remarkable properties which are inherent in nickel steel were not discovered until later, after the development of heat treatment. A more complete description of nickel steel was given by Colby in 1903.²

There are no particular difficulties attending the manufacture of nickel steel, and the open hearth, crucible or electric furnace can be used for the purpose. Nickel steel is freer from segregation than carbon steel, and, as it is an expensive metallurgical product, great care is exercised to eliminate gases, slag, etc., in order to produce a uniform and high-grade material. There is nothing about the element nickel, however, to assist in producing good steel, with the exception of its minimizing segregation.

Nickel steel can be forged and welded as readily as carbon steel, the only difference being that nickel steel commences to fuse at a lower temperature than the corresponding carbon steel, so that greater care must be exercised in heating. Heyn and Bauer

¹ *Journ. Iron and Steel Inst.*, 1889, No. 1, p. 45.

² *Mech. Eng.*, 1903, Vol. 12, p. 607.

found, for example, that a steel with 5.5 per cent. nickel must be handled very carefully on account of the danger of hot-shortness which is found in the neighborhood of 1100°C.¹ The most serious disadvantage of nickel steel is its liability to show seams and surface defects in the finished product. These imperfections can be at least partially eliminated by exercising greater care during refining, deoxidization and pouring.

The Iron-Nickel Constitution Diagram.—There have been no accurate determinations published of the freezing and melting points of the commercially important iron-carbon-nickel alloys, or

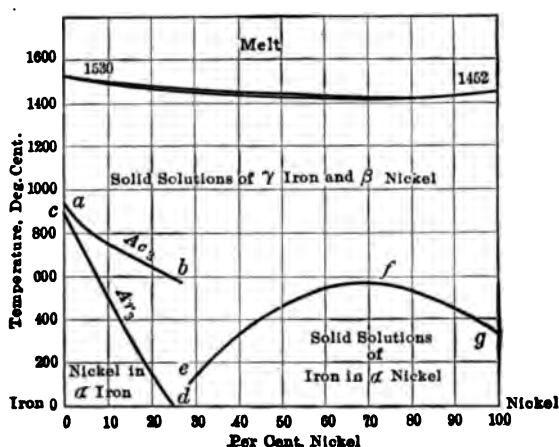


FIG. 114.—The iron-nickel constitution diagram.

the nickel steels. It is, however, well known that nickel lowers the melting point of iron and, presumably, of steel and it is to be hoped that determinations of the ranges of the commercially important steel compositions will soon be available. At present the best insight into the constitution and behavior of the nickel steels is to be had from a study of the work which has been done on the binary alloys of iron and nickel.

In Fig. 114 is given the iron-nickel diagram as determined with alloys containing only small amounts of carbon. The freezing points are those given by Guertler and Tammann² and confirmed by Ruer and Schüz.³ This diagram is of type I-b, with a minimum at 1425 to 1435°C. and 70 per cent. nickel, and shows that

¹ *Stahl u. Eisen*, 1909, Vol. 29, p. 632.

² *Zeit. anorg. Chem.*, 1905, Vol. 45, p. 205.

³ *Metallurgie*, 1910, Vol. 7, p. 415.

iron and nickel are soluble in all proportions in both the liquid and the solid states.¹ The minimum on the liquidus, in combination with the maximum at f on the transformation curve, suggests the possibility of the formation of a compound FeNi_2 . Electrical conductivity measurements, which should give the most positive indication of a compound in this region, are entirely too meagre to settle the point. The work of Burgess and Aston (1910) included only one alloy in this range. The specific volume-concentration curves of Chevenard show no anomaly for 0°C ., although for 750°C . the compositions FeNi_2 and Fe_2Ni come at the intersection points of three straight lines. Chevenard also noted that the reversible anomaly on the coefficient of expansion (α)—temperature curves gradually disappeared as the composition approached the composition FeNi_2 (67.75 per cent. Ni.) From these considerations it seems likely that FeNi_2 forms from the melt but that it undergoes a transformation just below 600°C . during which it also dissociates.² Further work will be required to settle this point finitely.

Transformations of the Iron-Nickel Alloys.—All of the work done on the transformations of the iron-nickel alloys shows that we have to consider at least two series of alloys. The alloys of the first series are called “irreversible,” after Osmond, by which is meant that they transform at appreciably higher temperatures on heating than on cooling. The transformation which takes place in these alloys undoubtedly corresponds to the A_2 transformation of pure iron and the exaggerated hysteresis is due to the sluggish action of the nickel on the crystallographic inversion. The alloy with 25 per cent. nickel remains non-magnetic on cooling down to room temperature, which shows that the transformation is completely suppressed by this amount of nickel. By cooling below room temperature this alloy regains its magnetism, which it then retains until it is again heated above 520°C .³ In connection with the transformation points

¹ The somewhat peculiar observation was made that the iron-nickel alloys solidify and melt at practically constant temperature, similarly to pure substances. This observation offers a rational explanation of the fact that nickel does not “segregate” in steel.

² *Rev. de Met.*, 1912, Vol. 11, p. 841.

³ HOPKINSON, *Proc. Roy. Soc.*, 1889, Vol. 46, and 1890, Vol. 47. The irreversibility of these transformations was also noted by LE CHATELIER, *Compt. Rend.*, Vol. 90, p. 285.

shown in Fig. 114, it should be noted that these lines do not give ranges in temperature over which the transformations take place nor the partitioning of the nickel in the two phases.

As a matter of fact, the study of meteorites, which are largely iron-nickel alloys, teaches that nickel is soluble in iron at room temperature only up to 6 to 7 per cent. This iron-rich solid solution is the constituent of meteorites known as kamacite. Any excess nickel above this amount forms a nickel-rich solid solution, known as taenite, which forms an eutectoid with kamacite, known as plessite (Osmond-Roozeboom theory).¹ As ordinarily made the iron-nickel alloys cool rapidly enough to allow only the A_3 reaction to take place and to suppress the eutectoid inversion.²

For practical purposes we may take the curves given in Fig. 114 as representing the transformation temperatures of the iron-nickel alloys. They were determined by Honda and Takagi and agree fairly well with other determinations of these points. The A_2 transformation is also lowered by the addition of nickel, although at a less rapid rate, and at about 8 per cent. nickel, it unites with the A_3 transformation.³ Points on these curves were determined by means of magnetization-temperature curves.

As the amount of nickel increases above 30 per cent., assuming cooling to room temperature only, the transformation takes place at the same temperature on cooling as on heating. These alloys are called "reversible." The transformation temperature increases to a maximum at about 70 per cent. nickel, above which

¹ The stability of the structures found in meteorites has been questioned by FRAENKEL and TAMMANN, who found that the duplex structures are converted into the simple polygonal structure, customarily found in these alloys, by heating to 400°C. (*Zeit. anorg. Chem.*, Vol. 60, p. 416). This assumption is not conceded by GUERTLER who points out that the transformation to plessite is so sluggish that it does not ordinarily take place. (*Zeit. physikal. Chem.*, Vol. 74, p. 428.) GUERTLER's contention is also supported by BENEDICKS who synthesized plessite by cooling a 12 per cent. nickel alloy very slowly to room temperature. (*Rev. de Met.*, 1910, Vol. 7, p. 1084.)

² On further thought, there remains the possible effect of the condition of homogeneous equilibrium in the melt produced by high superheating. Thus in all the cases recorded so far, plessite has been found only in alloys which have been heated in the liquid state to very high temperatures. Meteorites certainly were once at a very high temperature while BENEDICKS used the alumino-thermic method of preparing his synthetic meteoric iron.

³ HONDA and TAKAGI, *Journ. Iron and Steel Inst.*, 1919

composition it again decreases to the magnetic transformation of pure nickel. Honda and Takagi have shown that alloys with 30 per cent. nickel and above become "irreversible" when cooled to the temperature of liquid air. This irreversibility is supposed to extend to about 70 per cent. nickel. The thermal evidence, based on the results of magnetic analysis, may certainly be held to support the Osmond-Roozeboom theory but it must be remembered that the identification of the phasial successions leaves considerable to be desired.

Transformations of the Nickel Steels.—It was early shown by Osmond that nickel lowers all three critical points of steel, some-

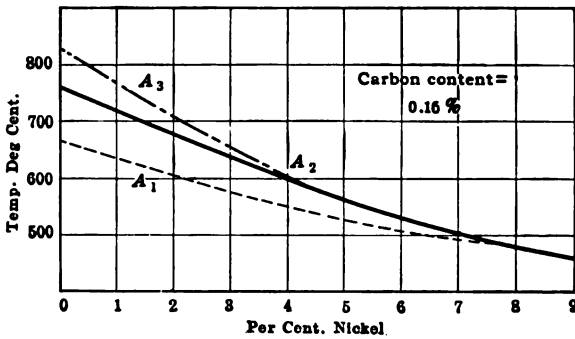


FIG. 115.—Effect of nickel on the critical points of steel. (Osmond.)

what as is shown in Fig. 115. Above 8 per cent. nickel, all three points are united. The critical points of a series of nickel steels used by Guillet in an early study of these alloys, are given in Table 82. These points were determined by the thermo-electric method.¹ Carbon is known to have a marked effect on the critical points, while manganese also has its effect and retards the transformations. Chromium, which is sometimes added to improve the physical properties, in itself does not have much of an effect but it intensifies the effect of carbon.²

The micrographic method employed by Goerens and Meyer³ has been applied in the same way to the determination of the

¹ BOUDOUARD, *Rev. de Met.*, 1904, Vol. 1, p. 80.

² DUMAS, *Journ. Iron and Steel Inst.*, 1905 No. 2, p. 255. How much of the effects described in the foregoing is to be ascribed to carbon and manganese, is not known, but it is to be regretted that the careful work of HONDA and TAKAGI was done on samples results were not accompanied by cor-

³ *Stahl u. Eisen*, 1910, Vol. 30

TABLE 82.—THERMO-ELECTRIC CRITICAL POINTS OF NICKEL STEEL

Composition		Critical points	
Carbon	Nickel	On heating	On cooling
0.070	2.23	860-775-725 weak	830-710 weak
0.125	5.23	770-695	710
0.220	4.70	750-800	600-650 (a)
0.125	7.13	760-690	650
0.132	10.10	725-660	565
0.125	12.07	680	400
0.110	15.17	660	360
0.176	20.40	480	160
0.160	25.85	410	
0.120	30.00		
0.800	2.20	705	695
0.776	4.90	675	625
0.815	7.09	665	560 weak
1.050	9.79	625	
0.760	12.27	625	
0.796	15.04	590	
0.800	20.01	560	
0.790	25.06	515 weak	
0.810	29.96		

(a) Hopkinson, *loc. cit.* These temperatures are the magnetic transformation points for $H = 0.12$ C.G.S. units. Blank spaces indicate no heat effects were observed.

critical points of the pearlitic nickel steels.' The effect of nickel on A_{r_3} is shown in Table 83.

TABLE 83.—EFFECT OF NICKEL ON THE CRITICAL POINTS OF STEEL

Per cent. nickel	A_{r_3} lowered to				A_{r_3} lowered by, °C.
	For 0.20 per cent. C	0.30 per cent. C	0.40 per cent. C	0.50 per cent. C	
1.0	850	842	830	811	32
2.0	817	809	797	778	65
3.0	782	774	762	743	100
4.0	742	734	722	703	140
5.0	697	689	677	658	185

—This table holds for 0.60 per cent. Mn.

l. 34, p. 1395. In this article a series of tables is carbon content and giving the proper annealing gases and nickel contents.

Certain of the micrographic determinations were checked and found to give correct indications by physical tests made on bars annealed at increasing temperatures.

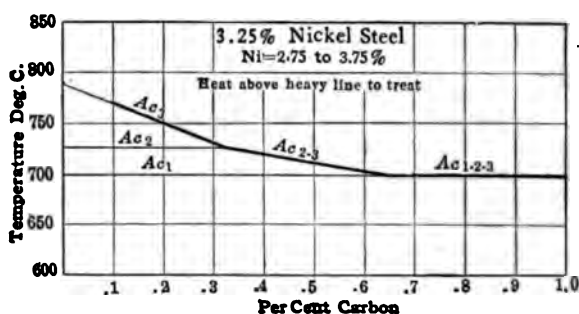


FIG. 116.—Critical points of 3.25 per cent. nickel steel. (*Midvale Steel Co.*)

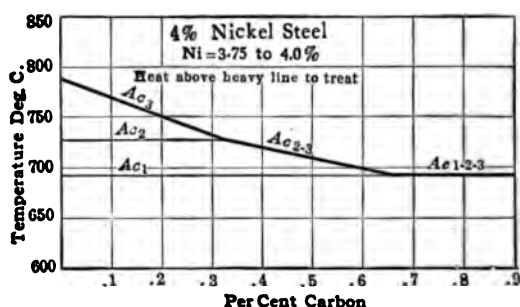


FIG. 117.—Critical points of 4 per cent. nickel steel. (*Midvale Steel Co.*)

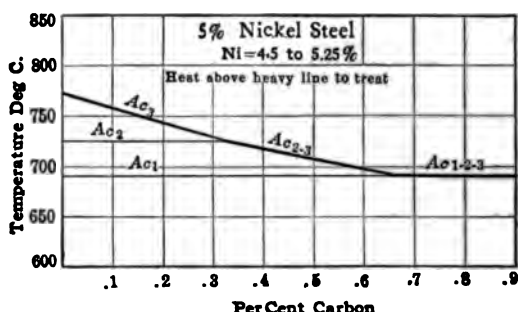


FIG. 118.—Critical points of 5 per cent. nickel steel. (*Midvale Steel Co.*)

The critical points of several commercial grades of nickel steel are given in Figs. 116, 117, and 118. The upper line is said to give the beginning of Ac_3 and, by making the proper allowance, these diagrams can be used in the heat treatment of these grades of

nickel steel. These results were obtained by the Bureau of Research of the Midvale Steel Company. The end of Ac_3 comes probably about 15°C . above the temperatures given.

Temperatures corresponding to the end of Ac_3 can be obtained from Fig. 119, which is given by Scott of the Bureau of Standards.¹ In addition Scott writes that Ac_1 is lowered by 10.5°C ., Ar_1 by 21.5°C . and that the eutectoid ratio is decreased by ca 0.042 per cent. for each 1 per cent. of nickel added.

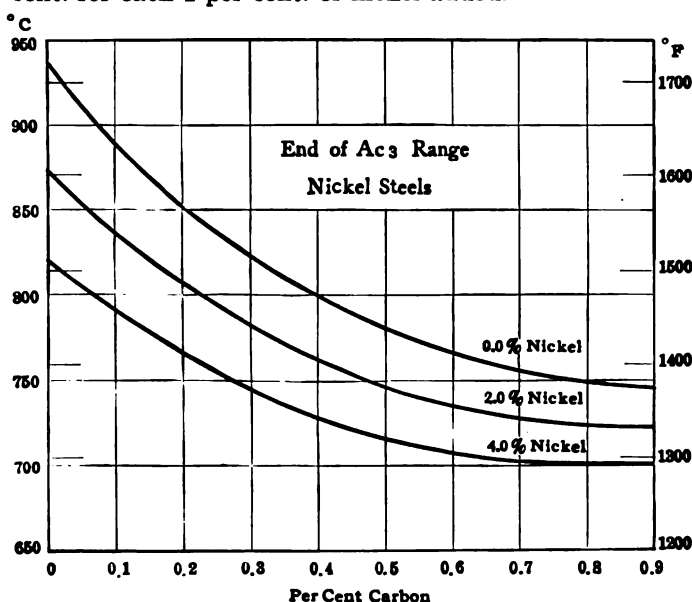


FIG. 119.—Effect of nickel on Ac_3 . (Scott.)

The Microstructure of the Nickel Steels.—The addition of nickel to carbon steels does not introduce a new constituent, as might be expected, but its effect is confined to suppressing the transformation points. This becomes perfectly apparent from an examination of the microstructure of the slowly cooled steels. This effect increases with both nickel and carbon and is to produce first martensite and then austenite.² The work of Guillet will

¹ "Critical Ranges of Some Commercial Nickel Steels." Amer. Inst. Min. Met. Eng., Feb., 1920, No. 158, Sect. 16.

² This had already been pointed out by OSMOND (*Comp. Rend.*, 1898, Vol. 126, p. 1352) who noted that the alloys containing up to 8 per cent. Ni were similar in structure to ordinary steel, but finer grained; those from 12 to 25 per cent. Ni were similar to quenched carbon steels; while the non-magnetic 25 per cent. alloys and those from 30 per cent. Ni up, had a simple polygonal structure.

be used as a basis for the study of the microstructure of these alloys because it is simple and comprehensive, and has been quite generally adopted.¹ The boundaries of the three fields, taken from the results of Guillet's investigations on ordinary forged steels are given in Fig. 120.²

The pearlitic steels have the same structure as ordinary carbon steels, *i.e.*, they consist of ferrite plus pearlite, pearlite, and cementite plus pearlite, according to the carbon content. The eutectoid ratio is shifted to lower carbon contents, by addition

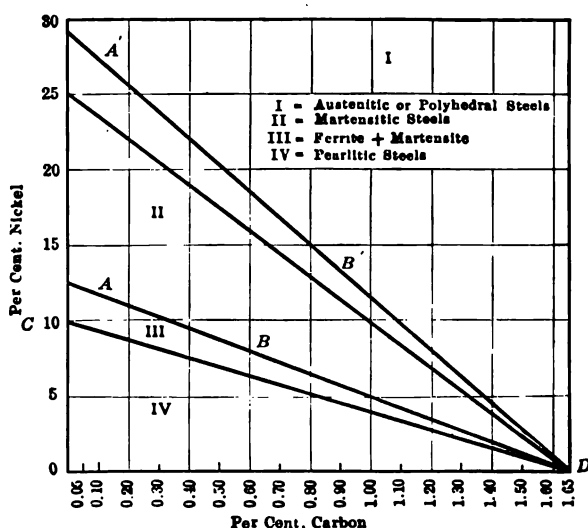


FIG. 120.—Diagram giving the microstructure of forged nickel steels. (Guillet.)

of nickel, so that it comes at about 0.65 per cent. carbon for 4 to 5 per cent. nickel. This effect of nickel in lowering the eutectoid ratio has been confirmed by thermal analysis (Scott). The significance of the eutectoid point is lost when an appreciable amount of nickel is added, on account of the smaller amount of segregation of the constituents, and the steels resemble granular pearlite more or less. This is quite pronounced on air cooling and the nickel steels have their strength and hardness increased by a greater amount on air cooling than the carbon steels do. The behavior of the pearlitic steels on quenching is the same as

¹ *Bull. d. Soc. d'Enc.*, 1903, May, p. 658; and *Genie Civil*, 1903, Vol. 43, p. 658.

² See GUILLET, *Alliages Metalliques*, 1906, p. 278.

of the carbon steels so that this point can be deferred until heat treatment is considered. With higher percentages of nickel, the nickel steels come in the class of special steels known as "air hardening" steels. The structure of these steels is sorbite, troostite or possibly ferrite plus martensite.

On further increasing the nickel or carbon, steels are obtained whose structure, upon ordinary unaccelerated cooling, is characterized by martensite. Strictly speaking the addition of nickel produces first the temper products and then the martensite although these subdivisions are not shown on the diagram.¹ In the zone marked ferrite plus martensite, the separation of ferrite causes an increase in the carbon content of the solid solution sufficient to limit its further transformation to martensite instead of to pearlite. The shifting or partitioning of the nickel during this transformation is not known. In low carbon steels this effect can lead to a false conclusion as to the carbon content from the microstructure. The grain is fine and the small patches of martensite give the appearance of (granular) pearlite (Hannemann). The difference between this martensite and the iron carbide of granular pearlite can be detected by etching with hot sodium picrate.

To sum up, we may state that the nickel steels on cooling form either pearlite, a temper product (generally assumed to be troostite) or martensite, or else they do not change at all. From the work of Boudouard² and of Carpenter, Hadfield and Longmuir³ it is evident that the effect of the addition of nickel is not continuous. With the first additions of nickel, pearlite is formed. As the nickel is still further increased, the temper product (troostite) is formed, while, with a still further increase in nickel, martensite is formed. The troostite formation has been called Ar', and the martensite formation, Ar'' (Scott). The results of Carpenter, Hadfield and Longmuir are represented by Fig. 121, which is due to Mr. Howard Scott of the Bureau of Standards. The steels represented contained 0.40 to 0.50 per cent. carbon and about 1 per cent. manganese and 0.16 per cent. silicon.⁴

¹ See GUILLET, *Rev. de Met.*, 1905, Vol. 2, p. 506.

² *Loc. cit.*

³ Seventh Report to the Alloys Research Committee; *Proc. Inst. Mech. Eng.*, 1905, Vol. 4, p. 857.

⁴ This effect has been studied in detail by Dejean: *Rev. de Met.*, 1917, Vol. 14, p. 641, and *Compt. Rend.*, 1917, Vol. 165, p. 429.

With still greater amounts of nickel and carbon, all transformation is suppressed and the steels are austenitic or polyhedral. Here the transformation comes below room temperature and a heat effect occurs neither on heating nor on cooling. The structure of a high-nickel or polyhedral steel is shown in Fig. 122. This photograph shows twinning, characteristic of γ iron, and a faint indication of a duplex structure. Certain anomalies in the microstructure of these steels will be discussed later.

The effect of nickel in precipitating free carbon is not given by this diagram, which obviously refers to combined carbon. High carbon and annealing at high temperatures tend to produce "annealing carbon." Waterhouse¹ reports 0.51 per cent. free

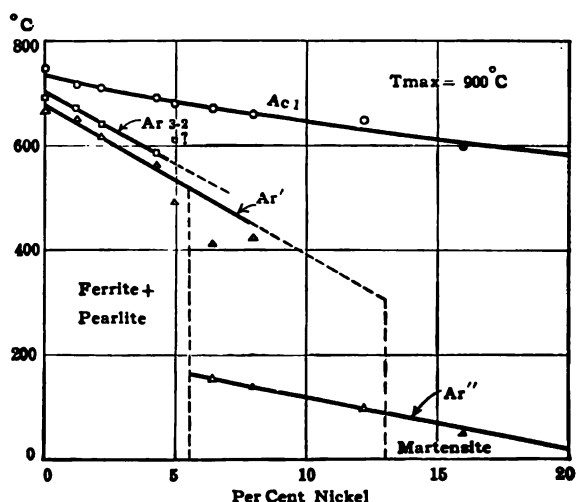


FIG. 121.—Critical points and structural changes in nickel steel. (Scott.)

carbon in a rolled bar containing 1.64 per cent. total carbon and 3.9 per cent. nickel and 0.80 per cent. free carbon in one containing 1.82 per cent. total carbon and 3.8 per cent. nickel. Annealing materially increased the annealing carbon. A steel with 1.24 per cent. total carbon and 3.8 per cent. nickel contained no free carbon, even after the annealing. In the series of steels recorded in Table 85 it will be noted that annealed 3 per cent. nickel steels with 0.67 per cent. carbon and above contain appreciable amounts of free carbon. The results of the heat treated bars show that this free carbon is dissolved during heating for

¹Iron and Steel Inst., 1905, No. 2, p. 386.

quenching so that this effect is not necessarily harmful in technical practice.

The carbide in nickel steel is generally assumed to be the simple carbide of iron, Fe_3C , following the work of Moissan¹ which indicates that nickel and carbon do not form a carbide. Ruff and Martin, on the other hand, found that nickel and carbon evidently form a carbide, Ni_3C , which was inferred from the maximum of the liquidus at this composition, but that it breaks down

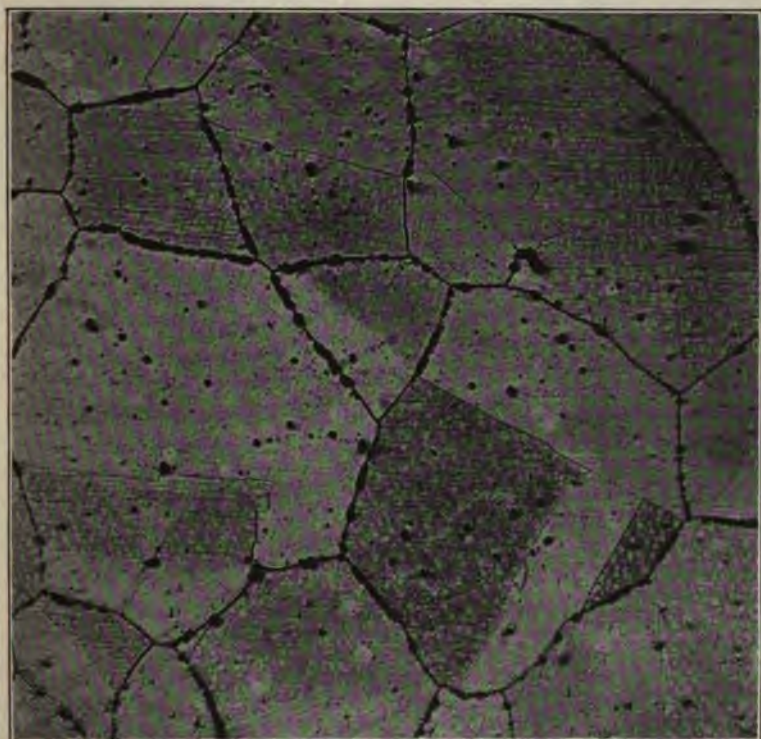


FIG. 122.—Structure of the irreversible, polyhedral nickel steels. Note twinning and secondary structure. (Foley.)

very rapidly into nickel and free carbon.² It is quite possible that some small amount of nickel dissolves in the Fe_3C , to form a double carbide of iron and nickel, but the physical properties of nickel steel indicate that the nickel goes principally to the iron to form nickeliferous ferrite. Waterhouse isolated by electro-

¹ The Electric Furnace, 1897.

² *Metallurgie*, 1912, Vol. 9, p. 143.

lysis and analyzed the carbide formed in his steels (containing 3.8 per cent. Ni) and found about 1.8 per cent. nickel to 91.7 per cent. iron and 6.3 per cent. carbon. This indicates that nickel can replace some of the iron in Fe_3C and it is undoubtedly this nickel that accelerates the graphitization.

The most authoritative statement of the composition of the carbide in nickel steel, low in manganese, is that of Arnold and Rhead.¹ The carbide of a cast bar containing 0.525 per cent. carbon, 3.25 per cent. nickel and 0.19 per cent. manganese was found to contain only 3 per cent. nickel. The authors drew the important deduction that "in ordinary (necessarily somewhat manganiferous) structural steels containing nickel, say, up to 7 per cent., the nickel is not associated with the carbon, but is alloyed with the iron and manganese." The authors state that in a steel with 0.8 per cent. carbon and 20 per cent. nickel, more Ni_3C than Fe_3C was found. This Ni_3C is said to be very unstable and to break down very easily precipitating graphite.

The Mechanical Properties and Heat Treatment of Nickel Steel.—The work of Hadfield² and Guillet³ has shown that it is the pearlitic nickel steels which are of greatest technical importance, although the austenitic steels, were it not for their great cost, have sufficiently valuable properties to indicate possibilities. According to this work we may divide these steels into three groups, as follows: (1) the pearlitic steels, whose properties correspond to those of the carbon steels, except that they are somewhat superior; (2) the martensitic steels having properties corresponding very closely to those of quenched steels and which are of little interest; and (3) the polyhedral steels with properties more characteristic of pure metals, such as copper, and simple solid solutions. The impact test brings out the three groups with exceptional sharpness, as the pearlitic and polyhedral steels are quite tough while the martensitic steels are fragile. It is interesting to note that the high carbon steels of the second and third groups show greater resistance to impact than the low carbon steels.

An idea of the properties of the pearlitic nickel steels in the forged condition can be obtained from Table 84.

¹ *Journ. Inst. Mechanical Eng.*, March, 1914, p. 248.

² *Proc. Inst. Civil Eng.*, 1898, Vol. 138, p. 1.

³ *Alliages Metalliques*.

TABLE 84.—PROPERTIES OF FORGED NICKEL STEEL

Comp.	T. S.			E. L.			Elong., per cent.			R. A., per cent.			B. H. No.			Res. to shock, mkg.		
% Ni =	0	2	5	0	2	5	0	2	5	0	2	5	0	2	5	0	2	5
C																		
0.12	49	51	56	38	39	42	23	23	24	70	73	75	85	135	185	36	35	33
0.20	59	61	69	39	42	51	23	22	20	62	59	60	100	150	160	23	22	18
0.80	...	128	142	...	65	85	...	18	10	...	24	24	205	240	250	4	4	4

T. S. and E. L. in 1000 lbs. per sq. in.

Elongation, gage length = $10 \times$ diameter.

Resistance to shock, Frémont test.

According to Abbott¹ a given amount of nickel produces the same change in the physical properties of steel, irrespective of the carbon content. The average effect of nickel in amounts up to 8 per cent. may be stated as follows:

0.01 per cent. of Ni increases the elastic limit 40 lbs. per sq. in.

0.01 per cent. of Ni increases the tensile strength 42 lbs. per sq. in.

0.01 per cent. of Ni increases the reduction of area 0.005 per cent.

0.01 per cent. of Ni decreases the elongation 0.010 per cent.

This shows that little is to be gained, in a commercial way, by adding nickel to steel if the material is to be used in the forged (non-heat treated) condition, and it is well known that nickel steel, in order to be commercially practical, must be suitably heat treated. This is because the superiority of nickel steel over carbon steel is brought out sufficiently to warrant the use of the more expensive nickel steel, only when it is in the heat treated condition. No detailed account will be made here of the properties of nickel steel because there are at present only a few standard grades in general use—principally those containing 3 per cent., $3\frac{1}{2}$ to 4 per cent., and 5 per cent. nickel.

The general effect of nickel on the properties of heat treated nickel steel has been given by Abbott for bars $\frac{3}{4}$ inch in diameter. The steel is assumed to have been quenched, *i.e.*, with a structure which is mainly martensite with no free ferrite, and the increase in strength, over that of carbon steel, on reheating to the temperature T, is as follows:

Addition of 0.01 per cent. Ni increases elastic limit by $287-0.174T$ lbs.

Addition of 0.01 per cent. Ni increases tensile str. by $294-0.214T$ lbs.

Addition of 0.01 per cent. Ni decreases elongation 0.0073 per cent.

Addition of 0.01 per cent. Ni decreases reduction of area 0.0073 per cent.

¹ The Role of Nickel in Alloy Steels, *Proc. A. S. T. M.*, 1917, Vol. 17, No. 2, p. 9.

TABLE 87.—PHYSICAL PROPERTIES OF 3.5 PER CENT. NICKEL STEELS

STEEL No. 2320

"Desired" composition: C 0.20 \pm 0.05; Mn 0.65 \pm 0.15; Ni 3.50 \pm 0.25

Reheating temp.		Tensile strength, 1000 lbs. per sq. in.	Yield point, 1000 lbs. per sq. in.	Elongation, per cent. in 2 in.	R. A., per cent.	Brinell hardness No.	Scleroscope hardness No.
°F.	°C.						
400	205	170	140	11.0	45.0	375	55
500	260	168	136	12.0	46.0	368	54
600	316	162	130	13.5	48.5	355	52
700	371	155	123	15.5	51.5	340	50
800	427	145	112	18.5	55.5	310	46
900	482	130	99	21.5	60.5	280	42
1000	538	112	84	25.0	65.5	240	38
1100	593	96	68	27.0	69.5	200	34
1200	649	82	54	29.0	72.5	165	31
1300	705	75	45	29.5	74.5	140	29
1400	760	70	40	30.0	75.0	125	28

Steel No. 2330

"Desired" composition: C 0.30 \pm 0.05; Mn 0.65 \pm 0.15

400	205	220	190	10.0	35.0	436	60
500	260	210	182	10.7	37.0	420	59
600	316	198	170	11.5	40.0	400	57
700	371	180	154	12.7	44.0	375	54
800	427	160	135	14.5	49.0	340	50
900	482	140	115	16.0	54.0	300	56
1000	538	120	95	18.0	59.0	250	41
1100	593	104	77	20.5	62.7	210	37
1200	649	92	64	22.5	66.0	180	34
1300	705	85	55	24.5	68.5	162	32
1400	760	80	50	25.0	70.0	150	30

Steel No. 2340

"Desired" composition: C 0.40 \pm 0.05; Mn 0.65 \pm 0.15

400	205	240	215	10.0	32.5	450	70
500	260	230	204	11.0	34.5	427	65
600	316	215	190	12.0	37.5	400	61
700	371	196	171	13.0	42.0	370	56
800	427	175	150	14.0	47.0	335	51
900	482	155	130	16.0	51.0	295	46
1000	538	135	110	18.0	55.0	260	42
1100	593	117	92	20.0	58.0	235	38
1200	649	105	78	21.5	60.0	215	36
1300	705	96	63	22.0	61.0	205	35
1400	760	90	60	22.5	62.5	200	35

Heat treatments: No. 2320. Heat to 1500–1550°F.—Quench—Draw.
 No. 2330 and No. 2340. Heat to 1500–1550°F.—Quench—Reheat to 1300–1400°F.—Quench—Draw.

The results obtained with a case hardened steel are reproduced from Bullens. The original steel analyzed: carbon 0.105 per cent.; manganese 0.43 per cent.; phosphorus 0.03 per cent.; silicon 0.11 per cent.; nickel 5.00 per cent.; after carburizing, the case ran 0.45 per cent. carbon. The steel was heat treated in the usual manner and it then possessed the following properties.¹

TABLE 88.—MECHANICAL PROPERTIES OF CASE-HARDENED NICKEL STEEL

	Tensile strength, lbs. per sq. in.	Elastic limit, lbs. per sq. in.	Elongation on 2 in., per cent.	R. A., per cent.	B. H. No.	Sclerometer No.	Res. shock
Core annealed. . . .	90,600	60,200	20	60.5	179	...	116
Core heat treated	200,000	170,000	12	54	295	...	75
Case heat treated.	260,000	250,000	2	5	490	74	

Nickel Steel Castings.—An interesting series of experiments on the annealing of nickel steel castings containing 0.10 per cent. to 0.50 per cent. carbon and 1.25 per cent. to 5.50 per cent. nickel was conducted by Meyer.² The correct annealing and hardening temperatures are given in tabular form for all the compositions met with in practice; this includes variations in carbon, nickel and manganese. The following table is given to illustrate the

TABLE 89.—EFFECT OF ANNEALING ON CAST NICKEL STEEL

Composition: C 0.24 per cent.; Ni 3.02 per cent.; Mn 0.44 per cent. Sound ingot.

Annealing temp., °C.	T. S., lb. per sq. in.	E. L., lb. per sq. in.	Elong., per cent.	R. A., per cent.	B. H., No.	Notch toughness	Grain size, μ^2
Unannealed	69,000	39,500	13.90	18.33	165.15	7.32	900
650	67,900	37,200	24.32	37.24	153.44	4.16	900
700	70,100	38,000	18.26	26.35	159.66	9.78	300
730	73,300	56,600	20.27	36.66	161.50	11.53	150
760	74,100	53,000	24.40	40.58	162.0	10.99	100
780	74,800	51,700	23.67	45.40	161.86	11.34	90
800	71,500	47,900	25.37	47.28	157.15	9.69	110
830	73,300	51,700	20.14	35.83	159.0	8.39	125
860	74,400	49,500	22.87	43.76	159.7	8.56	210
900	73,900	46,700	22.50	45.98	159.06	9.05	275
950	74,100	45,500	22.44	44.88	158.83	8.43	400
1000	74,400	43,500	23.06	45.73	157.55	7.98	575

Notch toughness is in mkg. per sq. cm. by the Charpy test.

Ratio of gage length to diameter in tensile bars was 10.

¹ The subject of case hardening will be considered in Part III.

² *Stahl u. Eisen*, 1914, Vol. 34, pp. 1395 and 1456.

effect of annealing temperature on the grain size and properties of nickel steel castings.

The results also brought out the value of using the correct annealing temperature and annealing time for the size and composition of the piece treated. Over-long annealing does much less harm at the correct annealing temperature than at higher temperatures. It is sufficient to heat small bars to the correct temperature and slowly cool without holding there any time. Steels with a larger cross section and higher nickel and manganese require a longer annealing time. When the steel is properly made and the annealing is properly conducted, the castings should approach forged nickel steel in quality.¹

Steels containing between 6 and 10 per cent. nickel, or high manganese with lower nickel, should be annealed by heating (drawing) to just below the transformation point on heating—400°C. to 600°C.

Effect of Low Temperatures.—Hadfield, in his classical work on the physical properties of steels at the temperature of liquid air, made the noteworthy discovery that the nickel steels are the only ones to retain their ductility at very low temperatures.² This effect is noticeable with the first additions of nickel while it is very pronounced in the polyhedral steels with 25 per cent. nickel.

Effect of Overstrain.—Nickel steel reacts to overstrain the same as carbon steel. The elasticity may be restored by treating the overstrained steel in boiling water although the nickel steels are slower in their recovery than carbon steel.³

Nickel steel can be used, although not always economically substituted, in place of carbon steels for practically all purposes and, when so, a considerable increase in strength and consequent saving in weight can be secured. There is an important condition which must be imposed here, as the writer has pointed out elsewhere,⁴ which applies with equal force to all similar special steels, which is that the design should be based upon the properties of the steel in question. If a special steel is used, where formerly a carbon steel was used, the special steel cannot possibly show to full advantage, particularly as regards cost, if the same

¹ CONE, *Iron Age*, 1913, Vol. 90, p. 287.

² *Journ. Iron and Steel Inst.*, 1905, No. 1, p. 147.

³ HANCOCK, *Phil. Mag.*, Vol. 6, p. 638.

⁴ *Journ. Amer. Soc. Mech. Eng.*, 1916, Vol. 38, p. 297.

design is used for both carbon and special steels. One of the principal features of the use of special steels is that they permit a change in design which brings greater efficiency, a saving in weight, longer life to the part and lesser wear and tear. Under certain conditions it might be well to use nickel steel, even though more expensive, as Waterhouse, in an article on its commercial uses, points out. Thus he states the battleships Rhode Island and New Jersey would lose 26 per cent. of their total weight of boiler tubes by using a 30 per cent. nickel steel, and besides a much less corrodible material would be secured.¹

The Physical Properties of Nickel Steel.—The early work on the magnetic properties² indicated that nickel suppresses the transformation points on cooling and that when 25 per cent. nickel is added the steel is ordinarily non-magnetic at room temperature due to the retention of γ iron, which here behaves as the solvent. With 30 per cent. nickel and over, the alloys are magnetic because the nickel, here acting as the solvent, transforms from its β into its α condition. Thus if either α iron, martensite, or α nickel forms on slow cooling the alloys are magnetic, while if γ iron and β nickel are retained, the alloys are non-magnetic. According to these ideas quenching from a high temperature should have no effect on the 25 per cent. nickel steel, *i.e.*, this composition should be non-magnetic in any condition as long as the temperature remains above room temperature. The effect of heat treatment on the pearlitic steels would depend upon the production of austenite or martensite, and if the former were produced (by quenching) the steel would be non-magnetic. The effect of heat treatment on the steels with 30 per cent. nickel and above would depend upon the possibility of suppressing the transformation point by rapid cooling.

Considerable light is shed upon these points by the work of Colver-Glauert and Hilpert, but at the same time this work indicates irregularities which can not be explained on the above grounds.³ Their results on two steels containing 0.37 per cent. carbon and 5.86 per cent. nickel, and 0.24 per cent. carbon and 24.32 per cent. nickel, respectively, are reproduced in Table 90.

¹ *Iron Age*, 1906, Vol. 77, Pt. 1, p. 490.

² HOPKINSON, *Loc. cit.* and DUMAS, *Loc. cit.*

³ *Journ. Iron and Steel Inst.*, 1911, No. 1, p. 375.

TABLE 90.—MAGNETIC PROPERTIES OF NICKEL STEEL

C 0.37 per cent.; Ni 5.86 per cent.				
Inducing force (H)	Quenched from 600°C.	Quenched from 900°C.	Quenched from 1240°C.	Slowly cooled from 1250°C.
0 (Retent)	9,600	9,100	8,900	6,500
8	5,100
10	1,800	580
11	700	7,000
13	0 (K)	0 (K)
25	7,700	2,000	1,000	6,200
28	0 (K)
35	0 (K)
50	13,500	5,800	7,100	12,900
75	15,400	10,100	11,300	15,100
100	16,450	12,450	13,400	16,300
150	17,800	14,550	15,550	17,600
200	18,700	15,800	16,900	18,500
300	19,900	17,400	18,650	19,750
400	20,850	18,700	19,900	20,700
450	21,250	19,100	20,400	21,000
300	20,300	17,850	19,000	19,700
150	18,400	15,550	16,500	18,150
100	17,350	14,300	15,200	17,100
50	15,900	12,550	13,100	15,450
10	12,150	10,000	10,200	10,100
0 (Retent)	9,600	9,100	8,900	6,500

C 0.24 per cent.; Ni 24.32 per cent.				
15	0	6.2	152.5	18.22
25	0	20	315	32
50	0	25	630	85
75	0	30	843	112
100	0	35	989	140
150	0	52	1,170	177
200	0	62	1,337	213
300	0	68	1,521	244

K = Coercive Force.

The authors considered their experiments to provide evidence against the usual assumption that austenite, when supercooled, is a non-magnetic material. This statement is rather broad in view of Maurer's non-magnetic austenite and is not even sub-

stantiated by the authors' own work, as shown in Table 90 for the 24 per cent. steel. The authors did show, however, that heating to temperatures above 900°C. produces fundamental changes in both the properties and microstructure, and that these changes are not obliterated by slow cooling although they tend to become so. The duplex structure noted in the 24 per cent. steel has not been explained but it shows that our present conception of this series requires modification.

The 33 per cent. alloy was only very slightly affected by thermal treatment; it was strongly magnetic and soft with the usual polygonal structure. The behavior of these alloys is evidently characterized by the nickel.

Other anomalies in the behavior of the non-magnetic alloys are to be found in the effect of mechanical working at room temperature. It is noted at once from the microstructure that the austenite grains are split up or fissured along the cleavage planes and that this is accompanied by a marked increase in hardness. This hardness is not greatly increased by cooling to below room temperature, which changes the austenite into martensite (Dumas). An even stranger effect produced by plastic deformation at room temperature is that the magnetic permeability increases to such an extent that the steel becomes magnetic, supposedly by the formation of martensite (Guillet).

The effect of nickel on the electrical resistivity of pure iron-nickel alloys shows a maximum of ca. 80 microhms per cubic centimeter at 28 to 35 per cent. nickel. The resistance drops off to 40 microhms at 22 per cent. nickel and 45 microhms at 47 per cent. nickel.¹ The relation between thermo-electric force of nickel steels and the nickel content is simple and in this way a check upon the chemical analysis is afforded.² In general, the thermo-electric properties of nickel steel check the other properties very satisfactorily. Minima occur in the thermoelectric power-temperature curves, for different carbon contents, at the concentrations corresponding to the martensite stage. The thermo-electric effects of these steels appear to be analogous to the ferro-magnetic effects, at least for those ranges of temperature

¹ BURGESS and ASTON, 1910.

² DEPUY and PORTEVIN, *Journ. Iron and Steel Inst.*, 1915, No. 1, p. 306; also *Compt. Rend.*, Vol. 155, p. 1081.

and concentration over which the phase constitution is the controlling factor.^{1, 2}

High Nickel Steels.—High nickel steels containing 25 per cent. nickel and above are seldom used except for special purposes such as for seamless tubing, valve stems for internal combustion engines, and other purposes for which non-corroding metals are required, and as resistance wire, containing 0.7 to 0.9 per cent. carbon and 25 per cent. nickel with about six times the resistance of pure iron, in the construction of rheostats.

Two special alloys were discovered by Guillaume while determining the coefficients of expansion of the steels used by Dumas,—one, known as "Invar," with a negligible coefficient of expansion, and another, known as "Platinite," with a coefficient of expansion equal to that of platinum or of glass.³ Invar contains about 36 per cent. nickel, and is now used extensively in chronometers, geodetic apparatus and scientific instruments of all kinds where it is sought to diminish temperature effects to a minimum. Those especially interested in this alloy should refer to Circular of the Bureau of Standards, No. 58, "Invar and Related Nickel Steels," 1916, which also contains a bibliography.

COBALT STEEL

The effect of cobalt on the properties of steel is surprising in that, in spite of the similarity between cobalt and nickel, the action is not at all pronounced. For this reason the ternary cobalt steels are not used.

Cobalt and carbon form a carbide Co_3C which forms to a

¹ See for example, HILPERT and HERMANN, *Zeit. Electrochemie*, 1913, Vol. 19, p. 215.

² It may be of scientific interest to note that, in accordance with the general deductions of SCHENCK, the ratio of the electrical and thermal conductivities of these alloys does not remain constant (HONDA). In the pearlitic range, each per cent. of nickel increases the resistivity approximately 2 microhms.

³ In an early paper, GUILLAUME noted that steels with 35 to 36 per cent. Ni expand ten times less than platinum (*Compt. Rend.*, 1898, Vol. 126, p. 738) and in later papers methods of heat treating or "aging" this alloy were discussed showing how it is possible to improve the properties still further. (*Compt. Rend.*, 1911, Vol. 153, p. 156). The minimum in the contraction curve at 36 per cent. Ni corresponds to a maximum concentration curve for 0°C. (CHEVENARD, *Compt. Rend.*, p. 5; also *Rev. de Met.*, 1914, Vol. 11, p. 841).

small extent in solution in Fe_3C .¹ Arnold and Read found that in steels containing about 20 per cent. cobalt, only 5 to 6 per cent. of the total cobalt is present as Co_3C and that the remainder is in solution in the ferrite. In drastically annealed steels the carbon is present as graphite on account of the action of the cobalt.

The addition of cobalt to steel, in the forged condition, has only a small influence in raising the tensile strength and lowering the elongation (Guillet) which can be partly accounted for by the fact that cobalt steels containing as much as 50 per cent. of cobalt remain pearlitic.²

COPPER STEEL

Copper steel has not been extensively used, although its properties have been well known for sometime. Copper was originally considered to be harmful in steel, principally because it was supposed to produce red shortness.^{3,4} More modern investigations have shown, however, that copper does not necessarily have a bad effect but that when added in small amounts to steel it improves the properties much as nickel does. Metallurgically, copper has a strong tendency to produce blow holes and except when the copper is low, it is difficult to secure a thorough mixture of copper and steel.⁵

From early experiments with copper-iron alloys and copper steel, it was concluded that copper and iron liquate in the liquid state into two immiscible layers, and that this liquation is increased by the presence of carbon. For example, according to

¹ ARNOLD and READ, *Proc. Inst. Mech. Eng.*, 1915, Vol. 25, p. 282. RUFF and KEILIG, *Zeit. anorg. Chem.*, 1914, Vol. 88, p. 410. For the constitution of the Co-C system, see BOECKEP, *Metallurgie*, 1912, Vol. 9, p. 296.

² GUILLET, *Alliages Metalliques*, p. 369; *Rev. de Met.*, 1905, Vol. 2, p. 348. This effect of cobalt on the properties of steel had already been noted by DUMAS and HADFIELD.

³ See for example, PERCY's "Iron and Steel," 1864, p. 147.

⁴ It was pointed out by Prof. T. TURNER at the Glasgow meeting of the Iron and Steel Inst., 1901, that copper in iron ores occurs as the sulphide, the sulphur of which is found in the finished steel and is responsible for the red shortness instead of the copper; see also *Journ. Iron and Steel Inst.*, 1882, No. 1, p. 369, describing the experiments of WASUM who found that copper did not produce red shortness which was due instead to sulphur.

⁵ See for example, HOWE, "The Metallurgy of Steel," 1890, p. 368.

Pfeiffer,¹ who examined the iron-copper alloys by thermal and microscopical analysis, iron and copper, and iron, carbon, and copper do not form true alloys, and the effect of copper on steel is due to the presence of copper in more or less finely divided particles in suspension.

Later work has shown that iron and copper are soluble in all proportions in the liquid state but that, when carbon is added, two liquid layers form. The width of the gap in liquid miscibility increases with the carbon. In the solid state, small amounts of copper remain in solution in the ferrite.² According to Stead, the solubility of copper in iron is lowered by carbon, but there can be no doubt that the amounts of copper ordinarily found in steel are in solution, contrary to the conclusion of Pfeiffer. Copper in amounts exceeding 2 per cent. can not be added to steel with any success (Wigham, Breuil).

The Critical Points of Copper Steel.—Copper affects the critical points of steel, qualitatively, the same as nickel does, but to a lesser degree (Osmond, 1890). This effect is limited, inasmuch as the critical points are not lowered below 550°C., according to Breuil,³ although his published curves are somewhat difficult to interpret. To give an average figure we may say that 1 per cent. copper lowers Ar_1 by about 10°C., and this point was found to come at 650°C. at 5 per cent. Cu, in steels containing 0.45 per cent. to 0.6 per cent. C.⁴ The effect on the other points is not as clear, although Ar_2 is undoubtedly lowered. Copper steels are magnetic at room temperature (Breuil). Copper, like nickel, retards the formation of pearlite with the result that the carbide is more uniformly distributed throughout the steel.⁵

¹ *Metallurgie*, 1906, Vol. 3, p. 281.

² STEAD, *Journ. Iron and Steel Inst.*, 1901, No. 2, p. 104. SAHMEN, *Zeit. anorg. Chemie*, 1908, Vol. 57, p. 1, who states that a maximum of 3.5 per cent. Cu dissolves in solid iron; RUER and FICK, *Ferrum*, 1914, Vol. 11, p. 39, who found that between 1 and 2 per cent. Cu dissolves in iron at room temperature.

³ *Journ. Iron and Steel Inst.*, 1907, No. 2, p. 1; *Compt. Rend.*, 1906, Vol. 142, p. 1421 and Vol. 143, p. 346. The last paper contains the results of an extended series of heat treatments and mechanical tests. It is pointed out that the copper steels become more sorbitic with increasing copper and that they should be seriously considered as possible competitors of the nickel steels.

⁴ CLEVINGER and RAE, *Trans. Amer. Inst. Min. Eng.*, 1913, Vol. 47, p. 523.

⁵ STEAD, *Journ. Iron and Steel Inst.*, 1901, No. 2, p. 104.

Heat Treatment and Mechanical Properties of Copper Steel.

In view of the fact that copper is so generally held to be harmful, it is surprising that Colby,¹ in an exhaustive investigation, found that copper in amounts up to about 0.5 per cent. produced no harmful effects, and that his work has since been confirmed by numerous investigators.²

Stead and Evans,³ in a paper on the influence of copper on steel rails and plates, confirming the work of Colby and Lippin,⁴ showed that between 0.5 and 1.3 per cent. copper has no deleterious effect on either the hot or cold properties of steel, and that, in small quantities, it raises the tensile strength and elastic limit slightly but that it does not thereby make the steel liable to fracture under sudden shock.

Stead and Wigham,⁵ after an extended investigation into the effect of copper on steel for wire making, were led to conclude that copper in high carbon steel for wire drawing purposes should be avoided; but this did not apply to the smaller amounts of copper. They concluded with Williams⁶ that copper in steel retards corrosion.

In further work⁷ it was shown that in steel containing 0.5 per cent. or more of carbon it is not of practical value to use more than 0.6 per cent. copper and that copper to the extent of 0.25 per cent. is not disadvantageous in the manufacture of even the best grades of steel wire.

This work shows clearly that, what is the important point, copper in small amounts or in many cases in amounts up to 0.6 per cent. has no harmful effect on steel. On the other hand, the action of copper is similar to that of nickel and results rather in an improvement to the steel both by bettering the mechanical properties of steel and by increasing its resistance to corrosion. Later work in this field, which will be briefly reviewed, has only tended to confirm these conclusions.

¹ *Iron Age*, Nov. 30, 1889, p. 1; also *Journ. Iron and Steel Inst.*, 1900, No. 1, p. 412.

² For a very complete annotated bibliography, see CLEVINGER and RAE (*Loc. cit.*). STEAD has also given an historical review of copper in iron and steel in the *Journ. of West Scotland Iron and Steel Institute*, 1901, p. 4.

³ *Journ. Iron and Steel Inst.*, 1901, No. 1, p. 89.

⁴ *Ibid.*, 1900, No. 2, p. 551; *Stahl u. Eisen*, Vol. 20, p. 536.

⁵ *Ibid.*, 1901, No. 2, p. 122.

⁶ *Iron Age*, Nov. 29, 1900.

⁷ Wigham, *Journ. Iron and Steel Inst.*, 1906, No. 1, p. 222.

From investigations on the tensile properties of alloys of electrolytic iron and copper, a considerable improvement in properties is obtained by adding 1 per cent. of copper, while alloys containing up to 2 per cent. may be easily forged.¹ Breuil considered it established that "a copper steel remains commercially serviceable up to about 4 per cent. copper," and that, from the point of view of tensile strength and ductility, copper steels are equal to the nickel steels. When copper exceeds 4 per cent. the material commences to be red short. The recent work of Clevenger and Rae² and of Hayward and Johnston³ on forged and heat treated steels offers abundant evidence of the valuable properties of copper steel although it seems doubtful if the advantages are sufficient to warrant an extended use of these steels as substitutes for the nickel steels. The addition of a nickel-copper alloy seems to be more practical, which amounts to the substitution of a small amount of copper for some of the nickel. The amount of copper added in this way should be as great as possible, which is about 1 per cent. without introducing segregation or other harmful effects. These cupro-nickel steels have been made by the addition of Monel Metal to steel and the results seem to have been highly satisfactory.⁴ The Monel Metal contained about $2\frac{1}{2}$ parts of nickel to 1 part of copper which would produce a steel with 1 per cent. copper and $2\frac{1}{2}$ per cent. nickel or $3\frac{1}{2}$ per cent. nickel + copper. On account of the equivalency of the copper and the nickel, this steel should have the same properties as ordinary $3\frac{1}{2}$ per cent. nickel steel and, if anything, should be somewhat less expensive to make.

The work of Stead and Wigham, Breuil, and Burgess and Aston,⁵ shows that copper does not exert a very great influence on the conductivity of iron. Dillner⁶ found that the magnetic properties of iron are not greatly affected by 0.5 per cent. of copper.

¹ BURGESS and ASTON, *Trans. Am. Electrochem. Soc.*, 1909, Vol. 16, p. 241; also *Iron Age*, 1909, Vol. 84, p. 1476.

² *Loc. cit.*

³ *Trans. Amer. Inst. Min. Eng.*, 1918, Vol. 58, p. 722.

⁴ CLAMER, *Metal Ind.*, 1910, Vol. 8, p. 303; *Eng. News*, Vol. 64, p. 1224.

⁵ *Met. and Chem. Eng.*, 1910, Vol. 8, p. 79.

⁶ *Stahl u. Eisen*, 1906, Vol. 26, p. 1493.

MANGANESE STEEL

The first work on manganese steel appears to have been limited to compositions containing up to $2\frac{1}{2}$ per cent. manganese, above which the materials became excessively brittle. Many useful alloys were secured in this manner as we know from the contributions of the Terre-Noire Company, France. This company was also successful in producing a high-grade ferro-manganese for the manufacture of these steels.

To Sir Robert Hadfield is due the credit of having first produced what is now commonly known as manganese steel, one of his early papers on the subject being that of 1888¹ in which he gave a summary of his former papers. Hadfield's contribution lay in carrying out the brilliant conception that by adding more than $2\frac{1}{2}$ per cent. manganese by means of a high grade ferro-manganese a hard material somewhat like spiegeleisen could be obtained, but tougher and more ductile due to the lower carbon content. After much experimentation it was found that by increasing the manganese above the brittle range, or up to 9-14 per cent. a material was obtained whose properties were entirely new. This new steel is commonly referred to as "Hadfield's Manganese Steel," and will be described in detail in the following pages. Compositions of 16 per cent. and above contained too much carbon, $1\frac{1}{2}$ to 2 per cent., to be of any particular interest and it was impossible with the ferromanganese at hand to work with any lower carbon content.

Another discovery, equally important as that of the high manganese steels, was the method of heat treating this new steel in order to secure the desired toughness, namely, "water toughening," which consists in quenching the article in water from 900° to 1100°C. (lemon yellow). This process, applied to ordinary steel, would cause brittleness, cracking, and other defects.

Several cases were recited to show the great strength and ductility of manganese steel. One steel, containing 13.75 per cent. manganese, after quenching in water, possessed a tensile strength of 145,000 lbs. per sq. in. and an elongation of 50.7 per cent. on 8 inches. The peculiar hardness of manganese steel was noted as it was almost impossible to make headway in manganese steel in the ordinary drill press and yet at the same time

¹ *Journ. Iron and Steel Inst.*, 188°

the sample could be indented by a hammer, showing a certain kind of softness.

It was found that even comparatively small deformations produce permanent set. This may be said to be the weakest point of manganese steel and is known to produce a peculiar flowage when it is used in crushing machinery and other places. There was said to be a well-marked yield point at about 63,000 lbs. per sq. in. Under a stress of 30,000 lbs. per sq. in., manganese steel was strained permanently by 0.004 inches while the same load in ordinary steel would produce a deformation which would be hardly measurable. Relative to forging manganese steel, Hadfield pointed out that the ingots must not be overheated but that the material could be forged without much trouble provided that proper care is taken. Hadfield noted that manganese steel is very fluid and comparatively dense, but that it cools more rapidly than ordinary steel and has a greater contraction causing piping and settling in the molds. The paper is concluded by a list of references on manganese steel.

The Effect of Manganese on Iron and Steel.—It was early determined by Le Chatelier, in 1898, that iron and manganese form a continuous series of solid solutions, although the constitution diagram was not laid down until 1905 by Levin and Tammann.¹ It was noted that the crystals of the solid solution were all uniform and homogeneous, similar to pure iron.² This is also corroborated by the relative position of the liquidus and solidus which fall close together. The constitution diagram shows that the solidus and liquidus run as smooth curves from the melting point of manganese at 1247°C. (1245°C.-Heraeus and 1247°C.-Rumelin and Fick) to the melting point of iron at 1530°C.³ This tendency of iron and manganese to form solid solutions with each other is not lost even in the presence of carbon.

The effect of manganese on the critical points of iron and steel was determined in 1897 by Osmond.⁴ His determinations, as contributed by Guillet, are shown in Fig. 123.

Wüst found that each per cent. of manganese, up to about 5

¹ *Zeit. anorg. Chemie*, 1905, Vol. 47, p. 136.

² Too rapid cooling of the alloys may give the appearance of heterogeneity (ROSENHAIN).

³ See also RUMELIN and FICK, *Ferrum*, 1915, Vol. 12, p. 41.

⁴ *Compt. Rend.*, 1897.

per cent., lowers A_{r1} by 20 to 25°C. and that the hysteresis is increased by a slightly greater amount. Above 5 per cent. manganese, no heat effect was noted on cooling, and by microscopical examination it was noted that the pearlite was replaced by martensite and troostite.¹ These results are generally accepted as giving the effect of manganese on the critical points, but they really apply to steels containing appreciable amounts of

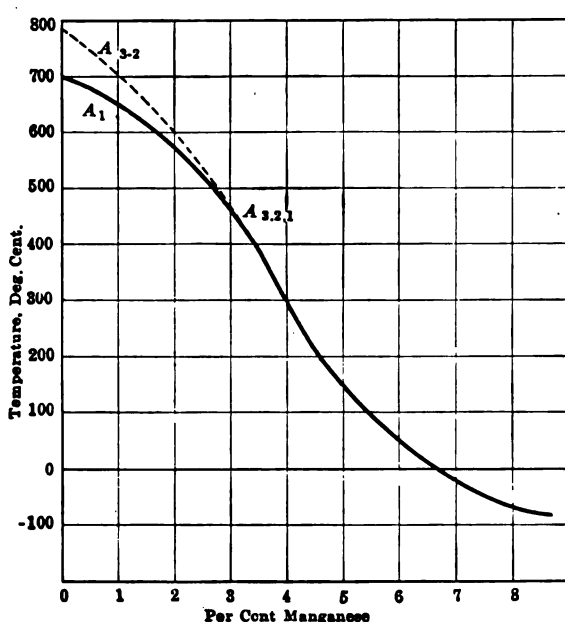


FIG. 123.—The effect of manganese on the critical points of steel. (Osmond.)

carbon. It is difficult to reconcile these results with those of Rumelin and Fick who found a heat effect at 816°C. from 1 to 50 per cent. manganese and another over the same range falling from 767°C. to 711°C.²

Manganese and carbon form a carbide, Mn_3C , containing 6.72 per cent. carbon which at high temperatures forms a continuous series of solid solutions with manganese. The liquidus passes through a maximum at 3.6 per cent. manganese at 1271°C., and the carbide melts at 1217°C.³ Quenched alloys show a solid

¹ *Metallurgie*, 1909, Vol. 6, p. 3.

² *Loc. cit.*

³ STADELER, *Metallurgie*, 1908, Vol. 5, p. 260 and 275.

solution structure between manganese and the maximum, and needle-like crystals between the maximum and the carbide. On slow cooling a second solid solution forms just below 900°C. The carbide Mn_3C was confirmed by Ruff and Gersten who described it as being soft (Mohs hardness = 1 to 2) and black and crystallizing as needles.¹ These same authors describe Fe_3C as being soft too, which makes their assertion regarding the hardness of Mn_3C highly doubtful. According to Hilpert and Paunescu, the alloys containing between 5 per cent. and 7 per cent. carbon are magnetic and soluble in dilute acids.² The manganese-carbon alloys have also been investigated by Ruff

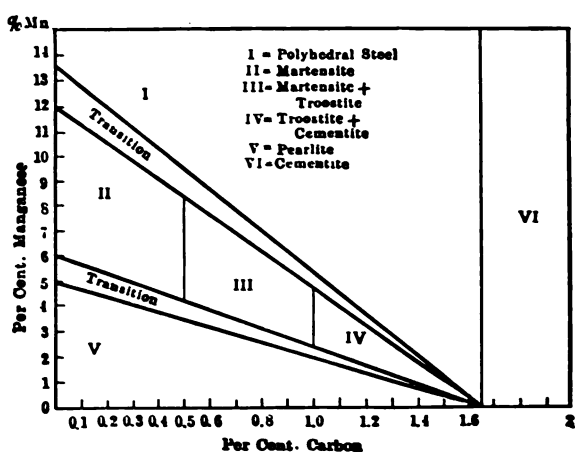


FIG. 124.—Microstructure of forged manganese steels. (Guillet.)

and Bormann to determine the equilibrium at high temperatures.³

Microstructure.—The first detailed description of the microstructure of the manganese steels was given by Guillet,⁴ whose classification, based on the structure of air cooled steels, is given in Table 91, and Fig. 124.

The steels with low carbon exhibited essentially the same structure as is met with in nickel steel, inasmuch as the low manganese steels were pearlitic while further additions of manganese produced first martensite and then austenite with transition zones between

¹ *Berichte*, 1913, Vol. 43, p. 400.

² *Berichte*, 1913, Vol. 46, p. 3479. In this paper some interesting carburizing experiments with methane are described.

³ *Zeit. anorg. Chemie*, 1914, Vol. 88, p. 365.

⁴ *Etude Industrielle des Alliages Metalliques*, p. 310.

TABLE 91

Microstructure	Steel with 0.20 per cent. C and	Steel with 0.80 per cent. C and
Pearlite.....	With 0 to 5 per cent. Mn	With 0 to 3 per cent. Mn
Martensite or troostite.....	With 5 to 12 per cent. Mn	With 3 to 7 per cent. Mn
Polyhedral structure.....	With over 12 per cent. Mn	With over 7 per cent. Mn

pearlite and martensite and between martensite and austenite. Guillet remarks that the polyhedra are not as perfectly developed



×100

FIG. 125.—Steel containing 10.7 per cent. manganese and 1 per cent. carbon quenched from red heat. Polyhedral structure. (Hanemann.)

in manganese steel as in nickel steel and that the regular markings on the surface are apt to lead to confusion in distinguishing between the martensitic and polyhedral steels. The structure of the austenitic steels is shown in Fig. 125.

In high carbon steels, containing about 0.8 per cent. carbon, it was noted that the pearlite was more compact and that it colored more readily on etching than ordinary pearlite does; that it approached more closely to sorbite in structure. On adding more manganese to these steels a structure corresponding to troostite was noted. From this it was concluded that no martensite would be found in the high carbon steels, the martensite

being replaced by troostite, or at least a constituent similar in appearance to troostite.

There is no marked difference between the ferrite of manganese steel and the ferrite of ordinary steel; in fact, the grain size, solubility and hardness are not affected by the addition of manganese. The effect of manganese on the pearlite point is known only in a general way; that is, manganese lowers the eutectoid composition. In 2 per cent. manganese steel the eutectoid comes at about 0.75 per cent. carbon, but here, again, the fining influence of manganese on the pearlite structure is similar to that of nickel and the exact location of the pearlite point is rendered more difficult.

The structures of manganese steel in a condition of stable equilibrium, as contrasted to the structures given in Fig. 124 for forged and air-cooled steels, are not known, but it seems highly probable that pearlite is the stable structure (leaving out of consideration the relative stability of cementite and graphite) at least up to the carbon and manganese contents of "manganese steel." This is based on the work of Potter who showed that the austenite of the polyhedral steels decomposes into troostite on heating,¹ and of Portevin, who obtained lamellar pearlite by cooling high-manganese steel from 1300°C. to 100°C. in 75 hours.²

The Carbide in Manganese Steel.—The composition of the carbide which occurs in pearlitic and austenitic manganese steel has been determined by Arnold and Read.³ Early work indicated clearly that the carbide in manganese steel contains manganese as well as iron and carbon, with the inference that the carbide Mn_3C of Moissan forms isomorphous solid solutions with the iron carbide.⁴ Before determining the carbides, the steels prepared were drastically annealed to precipitate all of the carbon as carbide. It was noted that, on the whole, the mechanical properties of this highly annealed series of steels do not differ materially from the unannealed alloys early described by Hadfield. The percentage of manganese in the carbide was found to increase with addition of manganese up to 20 per cent.

¹ *Trans. Amer. Inst. Min. Eng.*, 1914, Vol. 50, p. 437.

² *Compt. Rend.*, 1917, Vol. 165, p. 62.

³ *Journ. Iron and Steel Inst.*, 1910, No. 1, p. 169.

⁴ *STEAD, Journ. Iron and Steel Inst.*, 1894, No. 1, p. 191; and *MYLUS, FORRESTER and SCHOENE, Journ. Iron and Steel Inst.*, 1897, No. 1, p. 554. **GORDON** made this assumption or that manganese replaces iron in the

in the steel with 4 per cent. manganese. The authors remark that it is somewhat difficult to say whether the double carbides are true compounds or simply mixtures of iron and manganese carbides, so that it cannot be stated that the paper definitely proves the existence either of isomorphous mixtures of Fe_3C and Mn_3C , or of double carbides with definite chemical formulae. The assumption is usual that the former represents the true conditions. There is some indication of a carbide $3\text{Fe}_3\text{C}$, Mn_3C found in steels containing from 5 to 16 per cent. manganese but the difficulty of determining this point seems to be very great. Under the heat treatment of manganese steel we shall again consider the microstructure.

We have seen from this that manganese steel is very similar to nickel steel in its behavior on normal cooling. The first additions of manganese produce no phasial changes but merely affect the character of the ferrite + pearlite, or cementite + pearlite structures of carbon steel; further additions so retard the transformations of the solid solution that we have produced as normal, though not stable, constituents, martensite, troostite, etc., without the separation of graphite as in the nickel steels. Still further additions of manganese completely suppress the transformation of austenite by retarding the transformation or by lowering the A_{r1} point so that austenite, the solid solution, is the normal structural constituent. In this condition, manganese steel is non-magnetic.¹ In addition we have the carbide, or double carbide, which separates out of high-carbon steels, even though high in manganese, on slow cooling. As we shall see later on, it is possible to suppress the separation of this carbide by quenching the steel from a high temperature.

The Heat Treatment and Mechanical Properties of Manganese Steel.—The effects of the first additions of manganese to steel have already been considered in Chapter V. Although the low-manganese steels are not used to any great extent, it is now well known that manganese materially improves steel when present in amounts from 1 to 2 per cent. For example, Lang² found that each addition of 0.2 per cent. manganese increased the tensile strength by 2,133 lbs. per sq. in. and the hardness by about five points on the Brinell scale, and that both the hardness and ten-

¹ HADFIELD, CHENEVEAU and GENEAU, *Proc. Roy. Soc. (London)*, 1917, Vol. 94 A, p. 65.

² *Metallurgie*, 1911, Vol. 8, p. 15. See also STADELER, *Zeit. anorg. Chem.*, 1913, Vol. 81, p. 61, who arrived at the same conclusions.

sile strength were considerably higher in quenched steel than in annealed steels, the difference being far greater than in ordinary steel. Moreover, manganese up to 1.5 per cent. has no appreciable effect on the elongation and reduction of area. Quenched steels showed a martensitic structure but the carbon was too low to produce much brittleness. Manganese was found to increase the electrical resistance, which was, however, unaffected by heat treatment.

From the point of view of the properties of these low manganese steels, it would seem that their use should be more general, as a decided increase in strength is secured without incurring, at the same time, increased brittleness and fragility. The cost of these steels should not be very great, as compared to the improvement in properties. A manganese steel of this class containing 0.90 per cent. carbon and about 1.5 per cent. manganese has been used as a non-deforming steel.

The mechanical properties of high manganese steel in the cast and forged conditions and as affected by various heat treatments, were given by Hadfield in his original papers. The following table giving the tensile strength and elongation of a few typical samples is reproduced to show the effect of heat treatment on the properties of manganese steel.

TABLE 92.—MECHANICAL PROPERTIES OF MANGANESE STEEL

No.	Composition			Property	Heat treatment			
	C	Si	Mn		Forged	Cooled in		
						Air	Oil	Water
5	0.47	0.44	7.22	Tensile strength.....	60,400	60,400	56,000	56,000
				Elongation.....	2	5	3	2
13	0.85	0.28	10.60	Tensile strength.....	76,100	91,700	94,100	89,000
				Elongation.....	4	17	19	17
26	1.10	0.16	12.60	Tensile strength.....	87,200	82,800	112,000	123,200
				Elongation.....	2	11	28	27
22	0.85	0.28	14.01	Tensile strength.....	80,500	107,400	123,100	180,000
				Elongation.....	2	14	27	44
19	0.92	0.42	12.81	Tensile strength.....	89,600	106,000	127,000	125,000
				Elongation.....	6	20	33	37

Tensile strength in lbs. per sq. in. Elongation in per cent.

The quenching temperature
2000°F. or about 980 to
ment in properties by

is readily apparent, and has been explained more recently by microscopical evidence.

Regarding the heat treatment of manganese steel castings, Hadfield advised starting with a cold furnace and heating to an orange or lemon heat prior to quenching in cold water. This slow heating was devised for the purpose of eliminating heating strains which could very readily be produced in this material on account of its low thermal conductivity. Hadfield, somewhat later, advised heating the steel first slowly to about 800°C. and then rapidly to the proper quenching temperature.

The mechanical properties of manganese steel have also been investigated by Guillet¹ using two series of steels containing 0.034 to 0.396 per cent. carbon and 0.7 to 0.76 per cent. carbon. The results obtained were in close agreement with those of Hadfield. Guillet found that quenching the low carbon steels and the troostitic steels increased their hardness by producing martensite. Quenching the low manganese martensite steels had no effect on the hardness, while quenching the high manganese martensitic steels lowered the hardness by retaining them in the polyhedral condition. The polyhedral steels become softer by preventing the separation of free cementite.

The different classes of steels are brought out very clearly by the hardness test. The first additions of manganese produce a marked increase in hardness so that the steels containing from 5 to 7 per cent. manganese run from 400 to 450 in hardness on the Brinell scale, while the hardness of ordinary or high-manganese steel is around 200. However, this does not explain all about the hardness of manganese steel. As Hadfield early pointed out, manganese steel is peculiar in that it can be readily indented by a hammer but can be drilled or turned on a lathe only with the greatest difficulty. As has been demonstrated by practical experience with this material, resistance to abrasion primarily and its liability to deform plastically secondarily, are two of its chief characteristics.²

The mechanical properties of manganese steel as affected by heat treatment have been given by Potter,³ who attempted to

² Vol. 43, p. 261.

Experimental series of manganese steels, containing per cent. C. and from 1 to 20 per cent. Mn, have
KNOWLES, *Eng.*, Vol. 92, p. 478. The steels
and quenching.

Eng., 1914, Vol. 50, p. 437.

correlate the mechanical properties with the results obtained by heating and cooling curves and with the microstructure. Hadfield had already determined the cooling curve of manganese steel and found that no heat effect occurs, either on heating or on cooling, between 1300° and 200°C.¹ This work was apparently not known to Potter who again recorded cooling curves of manganese steel, although the curves given in his paper, are extraordinarily irregular and, therefore, unreliable. The secondary variations were so great that in one of them, No. 2, as many as nine heat effects were assumed by the author in a temperature range from 417 to 870°C. while if all the variations of equal order of magnitude were to be included, many more would have to be counted. This is of course highly improbable and the logical conclusion here is that manganese steel does not show a heat effect, as ordinary steel does, and therefore that the heat treatment can not be controlled by thermal analysis. The reasons for Potter's failure to secure reliable results from his thermal analysis lay obviously in the experimental method employed which was quite at variance with standard metallographical practice.

An interesting series of mechanical tests was conducted on round bars which had been quenched from the temperature of rolling and reheated for one hour to various temperatures, and again quenched in water. The best reheating temperature was found to be just below 900°C. which produced a tensile strength of from 150,000 to 160,000 lbs. per sq. in. and an elongation of from 42 to 65 per cent., as compared to 167,000 lbs. per sq. in. and 55 per cent. respectively for the original material. When the bars were held only five minutes at the reheating temperature, the best effect was obtained at about 950°C., the bars showing about 142,000 lbs. per sq. in. tensile strength, 53,000 lbs. per sq. in. elastic limit, and 56 per cent. elongation. The original material had an elastic limit of about 60,000 lbs. per sq. in. The difference between the original bars and the reheated and quenched bars was brought out clearly by the microscope which showed a somewhat coarser grain in the latter. The reheated bars which showed the maximum tensile strength and elongation corresponded in structure to uniform austenite of the finest grain size, but on the basis of the mechanical properties, nothing was gained by reheating. Heating to higher temperatures caused what the author calls "crackling" and the properties

¹ *Journ. Iron and Steel Inst.*, 1913, No. 2, p. 191.

deteriorated materially. This would indicate that the best heating temperature corresponds to a well-defined and fairly narrow range.

On reheating to temperatures just above 350°C. the austenite of the quenched bars was found to break down into a very fine structure resembling troostite. This breakdown corresponded to a very marked deterioration in the quality of the steel and the elongation dropped off to practically nothing. This effect continued up to about 760°C. At about this temperature and above, austenite began to form again, which, as soon as it again became uniform, gave the best results.

The effect of the separation of the carbide out of austenite on cooling, is very clearly brought out by his Table 3, and Fig. 13. A number of bars were all heated to 1150°C. and then cooled in the furnace at the rate of 55°C. per hour. Test bars were then drawn from the furnace at various temperatures and quenched in water. Down to 650°C. there was no change in the properties but the bar quenched at 593°C. showed a very great drop in elongation as well as in tensile strength. Under the microscope, it was seen that this bar was the first one in which carbide had separated out between the grains, and at the same time it was noted that the fracture was entirely intergranular, indicating a brittle cementing material. This series of tests shows clearly why it is necessary to quench manganese steel, which is to suppress the formation of the brittle cementite. This work also shows why it is that no heat effect is recorded when manganese steel is cooled because the separation of primary or free cementite never gives a definite heat effect and the austenite does not change into pearlite, as it ordinarily does.

In conclusion, the author remarks that steel containing 10 to 20 per cent. manganese and 1 to 2 per cent. carbon begins solidification at about 1370°C. and is for the most part frozen about 1270°C.; the eutectic freezes at 1125 to 1080°C. Regarding the possible separation of cementite out of the super-saturated austenite on heating, it was remarked that such an action takes place, and that this cementite is redissolved over the range from 725° to 870°C. with re-formation of austenite. Slight separation of a carbide also occurs at about 1025°C. as the melting point of the eutectic is approached. The tenderness of manganese steel between 1025° and 1125°C. is explained on the basis of this eutectic.

In the discussion it was pointed out by Hadfield that he had obtained his best results at temperatures as high as 940°C. or above the temperature mentioned by Potter. This might be explained as due to difference in composition or to preliminary treatment.

A study of the microstructure and of the heating and cooling curves of Hadfield, leads to the theory that manganese steel when cooling from a high temperature as homogeneous austenite, separates out the double carbide between the crystals of the solid solution, and that this is the only structural change which does take place under the usual conditions. On quenching, the A_{cm} line and the austenite + cementite field are passed through so quickly that the separation of the double carbide is inhibited, so that the solid solution is retained at room temperature in a supersaturated condition. In this condition it has mechanical properties corresponding to those of γ iron, especially as met with in nickel steels; *i.e.*, moderately low hardness, a high tensile strength but low elastic limit, and considerable ductility and toughness. This theory accounts very satisfactorily for the excessive brittleness and the slightly greater hardness of slowly cooled manganese steel as compared to the water-quenched steel.

Other work has dealt mainly with the constitution and magnetic properties of manganese steel although its importance, at present, is purely theoretical. Hadfield and Hopkinson, in a joint paper,¹ reported on the manner in which a normally non-magnetic manganese steel can be converted into a magnetic steel by reheating to temperatures below 700°C.² It was early known that this could be accomplished by heating manganese steel to a high temperature and cooling very slowly.

The temperature at which the maximum specific magnetism is obtained was not given in the paper but it undoubtedly lies at about 520°C. or slightly above. Heating at 700°C. rendered

¹ *Journ. Iron and Steel Inst.*, 1914, No. 1, p. 106.

² This was early reported by LE CHATELIER (*Compt. Rend.*, 1894, Vol. 119, p. 272) who found that the non-magnetic variety is transformed into the magnetic variety by reheating to 500 to 650°C., 550°C. giving the best results. The time required was about two hours and further heating to 800°C. produced the non-magnetic variety again. The electrical resistance of the two varieties was the same at about 730°C. being 1.79 ohms for a wire 1.4 mm. in diameter and 1 m. long; that of the two varieties at 15°C. was 0.83 ohms and 1.096 ohms. resp. See also, BRUSH, *Proc. Amer. Phil. Soc.*, 1918, Vol. 57, p. 344.

the material only slightly magnetic. Heating material which had already been made magnetic to temperatures exceeding 640°C. resulted in a diminution in the magnetism, until at 750°C. the loss is complete in a few minutes. Heating and cooling curves were taken of steel which had previously been made magnetic. Heat effects were recorded on the heating curves beginning at about 625°C. reaching a maximum at about 675°C. No heat effects were recorded on the cooling curves although it was remarked that on very slow cooling the magnetic change was undoubtedly accompanied by a heat effect.

On discussing the mechanical properties, it was noted that a heat treatment of water toughened steel which produced magnetism also renders the steel brittle and hard, as determined by the Brinell hardness test and by a bending test on small bars. The specific magnetism and hardness were seen to increase together but not proportionally, as if each property depended upon two or more variables. Pieces having even less than 1 per cent. of the magnetism of pure iron were decidedly brittle and were appreciably harder than water toughened manganese steel. For example, a bar annealed three hours at 650°C. had a specific magnetism of 0.2 ($\text{Fe} = 100$), a ball hardness number of 408, and bent through an angle of $2\frac{1}{2}$ degrees, as compared to 180 degrees for tough steel.

The microscopic examination of the steel so treated threw some light on the changes recorded but did not offer the final solution. Reheating water toughened steel to 400° for six hours apparently causes the separation of cementite plates, increases the hardness from 200 to 340, the specific magnetism to 0.2 per cent. and decreases the angle of bend to 12 degrees. Further heating increased the magnetism to 2 per cent. of that of iron and the hardness to 387 but apparently the austenite, or solid solution, remains unaffected. Reheating twelve hours at 520°C. or fifteen hours at 530°C. besides precipitating cementite plates, seems to produce at least a partial breakdown of the austenite and the ground mass is similar to troostite. The specific magnetism increases to 23 per cent., the hardness remains about the same, 387, while the angle of bend is 3 degrees. The hard network forming under these conditions was early observed by Stead¹ who undoubtedly considered it to be the double carbide of iron and manganese.

¹ *Journ. Iron and Steel Inst.*, 1894, Vol. 45, No. 1, p. 193.

The work has an interesting bearing on the effect of manganese on the critical points of the iron-carbon alloys. It was remarked that the A_1 point certainly lies above 650°C ., which means that manganese scarcely lowers the A_1 point but that, by retarding the transformation, it produces such hysteresis as to suppress it altogether. On this basis a simple theory may be established for considering manganese steel. Manganese added to steel has the effect, not of lowering the equilibrium temperature of austenite, ferrite, and cementite to below room temperature, but merely of inhibiting the transformation. On slow cooling, the carbon being above the eutectoid ratio, cementite separates out and we have cementite surrounding the austenite ground mass as envelopes. The austenite is metastable and is supersaturated with both iron and carbon. On rapid cooling, even the cementite segregation is suppressed. On excessively slow cooling, not only does cementite separate out but the transformation austenite = ferrite + cementite takes place to such an extent that a constituent probably corresponding to troostite or sorbite is formed. In the same way, reheating quenched manganese steel allows the austenite = ferrite + cementite inversion to take place and also permits the excess carbide to separate out.¹ Both of these doubtless produce a certain amount of magnetism; the latter is probably responsible for values up to about 1 per cent. of the magnetism of pure iron, while the former undoubtedly produces the higher magnetism which amounts to about 50 per cent. that of pure iron. The hardness doubtless increases with both steps, although the hardness and magnetism do not necessarily run parallel. This is because the austenite breakdown has a greater effect on the magnetism than it has on the hardness.

An apparent discrepancy here is the relation between the amount of carbide carbon and the magnetism, but this might be explained, as Professor Hopkinson does, by assuming that the determination of the carbon in the residue after solution in hydrochloric acid does not reveal the total amount of carbide carbon on account of some difference in the state of subdivision of the carbides. We would have such a difference in the decomposition products of austenite and the free carbide.

The behavior of manganese steel is also of interest from the point of view of the light which it throws on the allotropic

¹ This theory does not seem to offer a satisfactory explanation for the fact that two kinds of cementite form on heating.

theory of steel. Opposite views on this question seem to be held by Hadfield and Sauveur, the former believing that the phenomena observed neither substantiate, nor can be explained by, the usual allotropic theory. The contention is that when the steel becomes magnetic it also becomes harder and, if the presence of α iron be assumed to explain the gain in magnetism, it could hardly be called upon to explain the increasing hardness.¹ Sauveur,² who holds that the behavior of manganese supports the β iron theory, points out that the increase in hardness on reheating quenched manganese steel is undoubtedly due to the formation of β iron or martensite, β iron supposedly being a hard allotropic variety of iron. Sauveur explains that, on reheating, austenite changes partly into α iron, whence the magnetism, and partly into β iron, whence the hardness. On the basis of the theory advanced here, we would say that the increase in hardness is due to both cementite and troostite, both of which are known to be harder than austenite, and that the magnetism is due to troostite (and partly to cementite), which is supposed to contain α iron, although here the α iron would contain manganese in solution. The difference between Sauveur's theory and the writer's theory, is that the former calls for the formation of martensite on reheating, while the latter calls for troostite. To substantiate his claim, Sauveur published a photograph of a steel which had been reheated to 700°C. for two hours, said to be martensite. Among other reasons which negative this assumption, it can hardly be consistently assumed that martensite would remain as a stable structure for two hours at 700°C., for, otherwise, manganese steel in this condition would be an excellent high speed steel. The constituent in question is without doubt cementite, arranged in Widmanstaettian structure by its separation as a segregate in austenite. Apparently there is no possibility of austenite transforming into martensite on being reheated, and certain it is that no structure forms which produces the characteristic martensitic hardness.

The Hardness of Manganese Steel.—The Brinell hardness test gives a hardness number of about 200 for ordinary manganese steel, either slowly cooled or water toughened. Presumably, the ball hardness would be slightly greater for the slowly cooled

¹ HOPKINSON and HADFIELD, *Trans. Amer. Inst. Min. Eng.*, 1914, Vol. 50, p. 44.

² *Ibid.*, p. 501.

steel, due to the slight precipitation of carbide. Hadfield and Hopkinson¹ found that when reheated to temperatures below 500 to 600°C. the hardness increased very greatly, even as high as 450. Cold working or cold deformations have the same effect of increasing the hardness; thus, Hadfield and Hopkinson found a hardness of 490 for a broken test bar of water toughened steel. This is also borne out by hardness tests made on worn, or flowed parts of crushing machinery which show hardness figures up to 400 and above. Hadfield reports that the maximum hardness he has been able to obtain is not greater than 550 which is below glass scratching hardness which requires a ball hardness number of at least 600.

Physical Properties of Manganese Steel.—Manganese steel containing 14 per cent. manganese has eight times the resistance of iron and thirty times the resistance of copper (Hopkinson). Le Chatelier showed that each 1 per cent. increase in the manganese content increased the resistance by five microhms. The thermal conductivity is also less than that of ordinary steel; in fact, its low conductivity is responsible for the great care which must be exercised during heating and quenching manganese steel. It is even necessary at times to alter the design of patterns to produce castings which will be free from internal strains. If the metal added is not required in the finished casting, it is later removed by grinding. According to Potter,² the thermal conductivity of manganese steel up to 600°C. is about one-third that of ordinary carbon steel.

The Uses of Manganese Steel.—Manganese steel containing below 1.5 per cent. manganese is used in Europe, especially in Germany. With this amount of manganese the carbon content can be materially lowered, which has the effect of giving a better combination of strength and toughness than could ordinarily be secured. Railway materials requiring these properties run from 0.15 to 0.40 per cent. carbon and from 0.70 to 1.40 per cent. manganese. Shell steel runs from about 0.50 to 0.60 per cent. carbon, 0.70 to 0.90 manganese, with from 0.10 to 0.30 per cent. silicon although in cast steel shells of German origin, the author has found the silicon to be 0.50 to 0.60 per cent. Flasks to sustain high pressures are made of steel containing 0.25 to 0.30 per cent. carbon and 1.40 to 1.45 per cent. manganese. Steels containing

¹ *Loc. cit.*

² *Stahl u. Eisen*, 1909, p. 722.

up to 1.6 per cent. manganese were recommended as a wartime substitute for special steels in automobile construction.¹ The polyhedral manganese steels, which are commonly meant in this country by the term "manganese steel," are used for a great number of purposes whenever resistance to abrasion alone, or resistance to abrasion in combination with toughness is required. This question has been discussed by McKee, Vice President of the American Manganese Steel Company, in a paper on "Manganese Steel Castings in the Mining Industry."² A typical analysis given is as follows: C 1.25, Si 0.30, Mn 12.50, S less than 0.02, P about 0.08. The average mechanical properties of nineteen tests are tensile strength 108,500 lbs. per sq. in.; yield point 53,400 lbs. per sq. in.; elongation on two inches, 33.7 per cent.; reduction of area, 38.6 per cent.

Some of the common uses for manganese steel castings are as the wearing parts for rock crushers, tube mills, dredges, steam shovels, rolling mills, pumps, concrete mixers, etc. It is also used for gears, pinions, frogs, and cross-overs. As rolled, it is used as steel rails which are to be used principally on curves and where traffic is excessive. The use of manganese steel for rails has been the subject of special discussion, principally by Hadfield and Potter who, in their papers have brought out the peculiarities of this material and the method of treatment.³ One of the serious disadvantages attending the use of manganese steel rails is that the wheels are apt to slip. One railroad on this account, was obliged to return to carbon steel rails after trying manganese steel rails on a curve which came on a grade.

SILICON STEEL

Silicon affects steel in an entirely different manner from manganese, and while both are used in the construction of parts of machinery and equipment, the silicon steels are of importance on account of a different set of mechanical and physical properties.

Steels containing more than 7 per cent. silicon and practically no carbon can not be formed and resemble cast iron. While such alloys are used on account of their resistance to chemical

¹ JANOS, *Stahl u. Eisen*, 1918, Vol. 38, p. 567.

² *Trans. Amer. Inst. Min. Eng.*, 1916, Vol. 53, p. 437.

³ POTTER, *Stahl u. Eisen*, 1909, p. 721; BREUIL, Intern. Congress, Düsseldorf, 1910, sec. 2, paper 3; HADFIELD, *Trans. Amer. Inst. Min. Eng.*, 1914, Vol. 50, p. 327.

action, they are always used as cast. Contrasted to silicon steel we have manganese steel in which additions of manganese up to about the same amount produce brittleness, while further additions restore the ductility which is not true of silicon steel. Again, silicon does not destroy the magnetic properties of iron and steel as manganese does, as the 7 per cent. alloy is equally as susceptible as ordinary iron or steel. Up to about $1\frac{1}{2}$ to $1\frac{3}{4}$ per cent. silicon the elastic limit is raised without impairing the ductility; above this amount of silicon a further increase in tensile strength entails a serious loss in ductility; steel with $3\frac{1}{2}$ per cent. silicon is quite stiff and bends only to a right angle, and with about this amount of silicon, it is not possible to draw silicon steel into wire form. Steel with 2.67 per cent. silicon and 0.20 per cent. carbon can be easily drawn to #20 B. & S. gage, and in such condition has a tensile strength of 143,360 lbs.¹ Silicon is also detrimental to welding.

Constitution of Silicon Steel.—The work of Guertler and Tammann, and Gontermann has shown that iron and silicon form a compound FeSi. The addition of silicon to iron greatly lowers the melting point up to about 20 per cent. silicon, which is also the limit of solid solubility of silicon in iron.²

The effect of silicon on the critical points of iron and steel has been the subject of considerable controversy and a brief review of the literature will be given.

According to Osmond,³ silicon raises A_3 but lowers A_2 , the magnetic transformation. Baker⁴ found that 1.2 per cent. silicon eliminates Ar_3 from iron, confirming the work of Osmond and Arnold,⁵ and lowers the Ar_2 point about 7 to 9°C. per one per cent. silicon. A heat effect was noted at about Ar_1 but was not considered to be a eutectoid point. However, Guertler and Tammann found no appreciable effect on the magnetic transformation point by the addition of silicon up to 47.5 per cent. Undoubtedly more refined determinations of the magnetic

¹ See HADFIELD, *Journ. Iron and Steel Inst.*, 1889, No. 2, p. 222. This is the first important paper on silicon steel and indicates in a general way what is to be expected from the mechanical properties of these alloys.

² GUERTLER AND TAMMANN, *Zeit. anorg. Chem.*, 1905, Vol. 47, p. 163. GONTERMANN, *Ibid.*, 1908, Vol. 59, p. 373.

³ *Compt. Rend.*, 1890, Sept. 1; *Journ. Iron and Steel Inst.* 1890, No. 1, p. 38.

⁴ *Journ. Iron and Steel Inst.*, 1903, No. 1.
Journ. Iron and Steel Inst., 1894

transformation points, or the adoption of a uniform definition of the point, would eliminate these differences.

The effect of silicon on the transformation points of iron and low carbon steels has also been studied by Charpy and Cornu¹ by dilatation and cooling curves. By dilatation experiments on steel with 0.1 per cent. carbon and 0.30 per cent. manganese with silicon from 0.20 to 4.5 per cent., they found that the anomalies of the coefficient of expansion between 800 and 900°C. disappeared with 1.3 per cent. silicon so that the expansion between 0° and 900°C. was represented by a straight line, although silicon does not change the coefficient. With 0.35 per cent. carbon and 0.8 per cent. manganese at least 4.5 per cent. silicon was reached before the critical point was suppressed. The experiments were not conclusive, but they were taken to indicate that the A_1 and A_3 points were eliminated by silicon but that the A_2 point was not. Vigoroux² immediately thereafter published heating curves of a series of iron-silicon alloys containing up to 6.6 per cent. silicon, none of which showed A_1 or A_3 . A_2 was raised by the addition of silicon by about 28°C. for each per cent. of silicon up to 3 per cent., above which point the increase was more irregular. At 7 per cent. silicon A_2 disappeared.

As a result of the work of Vigoroux, Charpy and Cornu³ again determined the effect of silicon on the transformation points, this time by thermal analysis. With 1.5 per cent. silicon A_3 disappeared. The A_2 point was well-defined in all the samples and was lowered 11°C. for each per cent. of silicon. A_1 was slightly raised but disappeared at about 5 per cent. Some of the transformation points determined were as follows: 0.11 per cent. silicon, $Ar_1 = 660^\circ$; $Ar_2 = 740^\circ$; $Ar_3 = 820^\circ$. For 3.3 per cent. silicon, $Ar_{1,2} = 690^\circ$. For 0.35 per cent. silicon and 0.35 per cent. carbon, $Ar_1 = 630^\circ$ and $Ar_2 = 690^\circ$. For 4.2 per cent. silicon and 0.35 per cent. carbon, $Ar_1 = 714^\circ$ and $Ar_2 = 670^\circ$. The points coincide at 3.2 per cent. silicon but above this percentage A_1 occurs at a higher temperature than A_2 .⁴

¹ *Compt. Rend.*, 1913, Vol. 156, p. 1240.

² *Ibid.*, 1913, Vol. 156, p. 1374.

³ *Ibid.*, 1913, Vol. 157, p. 319.

in debated by VIGOROUX, and CHARPY and CORNU in
a note (*Bulletin d. l. Soc. Chim. d. France*,
on heating curves of his silicon steels and re-

In a later paper¹ Charpy and Cornu again discuss the effect of silicon on the critical points as determined by both thermal analysis and dilatation. They state that they have confirmed that silicon raises A_2 but diminishes its magnitude. A_1 rises with silicon until it first coincides with A_2 and then rises above A_2 until it finally disappears, whereupon all the carbon is in the graphitic form. A_2 falls with increase in silicon but does not vary in intensity.

The ternary alloys of iron-carbon-silicon have been studied by Wüst and Peterson,² but it was mostly cast irons which were considered. The complete ternary system from iron to Fe_3C and $FeSi$ has been determined by Gontermann, first preliminarily and then more completely,³ but here, again, but little of the work concerned silicon steel. Gontermann found a decided increase in A_1 with increase in silicon. In an alloy with 0.82 per cent. carbon and 7.7 per cent. silicon it occurred at about 900°C.

The constitution of high-carbon, silicon steels has also been determined by Schols.⁴ Silicon was found to lower the temperature of primary crystallization, as would be expected from the work of Guertler and Tammann, but the eutectic point remained constant at about 1120°C. Schols again found that the pearlite point is raised but that it disappears as the silicon is increased. In alloys containing 1.2 per cent. carbon this occurs at about 5.6 per cent. silicon, and with 1.5 per cent. carbon, at about 4.5 per cent. silicon. He found, as did Spiecker and Gontermann, that the solubility of carbon in γ iron was lowered with increase in silicon content.⁵ The eutectic point was found to enter at 1.2 per cent. carbon with 5.6 per cent. silicon, at 1.5 per cent. carbon with 1.8 per cent. silicon, and at

affirming his position. CHARPY and CORNU (*Ibid.*, p. 497) replied and pointed out that the probable reason for the failure of VIGOROUX to confirm the work of OSMOND, ARNOLD, STEAD and BAKER was to be found in his method of recording the critical points. It was noted, for example, that the curve for pure iron showed just one point at 726–746°C. and that only four minutes of time elapsed in heating from 650° to 900°C.

¹ *Journ. Iron and Steel Inst.*, 1915, No. 1, p. 276.

² *Metallurgie*, 1906, Vol. 3, p. 811.

³ *Journ. Iron and Steel Inst.*, 1911, No. 1, p. 421.

⁴ *Metallurgie*, 1910, Vol. 7, p. 644.

⁵ It has been suggested by ANDREW that the raising of the A_2 point by silicon may account for the insolubility of carbon in high silicon alloys. Carnegie Scholarship *Mem.*; *Iron and Steel Inst.*, 1916, Vol. 7, p. 1.

1.9 per cent. carbon with 1.1 per cent. silicon. This effect was verified by Charpy and Cornu,¹ who found that silicon gradually diminishes the solubility of carbon in iron and that for 4 per cent. silicon it becomes zero at 900°C. while for 7 per cent. silicon it becomes zero at 1000°C.

Hague and Turner have determined the intervals of solidification, eutectic points, and pearlite points in carbon-iron-silicon alloys by following the volume changes on cooling. Silicon varied from 0.03 to 4.83 per cent. and the total carbon from 2.26 to 2.29 per cent. The tests showed that the pearlite point was raised from 700°C. with no silicon to 795°C. with 5 per cent. silicon; the eutectic point was raised from 1130° to 1160°C. over the same range, while the first arrest, which indicated the commencement of solidification, was lowered. Hardness tests showed that the hardness increases up to about 1 per cent. silicon, but that as soon as the carbide carbon changes into graphitic carbon (1 to 2 per cent. silicon), a sudden drop occurs. Above 2 per cent. silicon, there is a gradual increase in hardness due to the increasing amount of FeSi in solution in the iron.

The first additions of silicon to steel produce no effect on the microstructure except to increase the grain size.² Silicon steel with 2 per cent. silicon is known to be quite coarse grained. Between 5 and 7 per cent. silicon the carbon is partly carbide carbon and partly graphitic carbon but above 7 per cent. silicon, all the carbon is present as graphite, while the ground mass is the solid solution of FeSi in iron. Above 20 per cent. the compound forms one of the two constituents of the alloy, the other being graphite.

The Heat Treatment and Mechanical Properties of Silicon Steel.—The general effect of silicon on steel has been given in the introduction, and may be summarized by means of Tables 93 and 94, the former taken from the work of Hadfield and the latter from the work of Wahlberg.

When considering the effect of silicon on the properties of steel, it must be borne in mind that (a) silicon is a powerful deoxidizer and "solidifier" and (b) its oxidation product, SiO₂, has a powerful effect on the properties of the finished steel. Consequently the properties of a given steel will depend very

¹ *Compt. Rend.*, 1908, Vol. 147, p. 901. See also CHARPY and CORNU, *Compt. Rend.*, 1913, Vol. 156, p. 1616.

² GUILLET, *Alliages Metalliques*, p. 355.

considerably upon the "condition" of the steel, both before and after the addition of the silicon, and the influence of the smaller amounts of silicon can be masked by variations in the metallurgical practice (Wahlberg).

TABLE 93.—MECHANICAL PROPERTIES OF SILICON STEEL. HADFIELD

Composition		Treatment	Limit of proportion, lbs. per sq. in.	Tensile strength, lbs. per sq. in.	Elongation, per cent. on 2 in.	R. A., per cent.
C	Si					
0.14	0.24	Not annealed	49,000	73,960	30.1	54.5
		Annealed	34,000	56,000	37.6	50.7
0.18	0.79	Not annealed	56,000	76,400	29.5	54.5
		Annealed	42,500	66,100	34.0	52.7
0.19	1.60	Not annealed	62,700	84,000	31.1	50.6
		Annealed	56,000	73,960	35.1	54.5
0.20	2.11	Not annealed	69,300	88,400	18.5	28.0
		Annealed	56,100	76,200	36.5	60.0

TABLE 94.—MECHANICAL PROPERTIES OF SILICON STEEL. WAHLBERG

Composition		Treatment	Limit of proportion, lbs. per sq. in.	Yield point, lbs. per sq. in.	Tensile strength, lbs. per sq. in.	Elongation, per cent. on 6 in.	R. A., per cent.
C	Si						
1.30	0.29	Not annealed . . .	78,900	80,400	123,742	6.7	10.3
		Annealed	54,700	55,800	92,100	19.4	45.2
1.30	0.60	Not annealed . . .	78,400	93,000	148,300	6.0	6.9
		Annealed	78,900	83,700	143,300	9.3	11.6
1.25	0.83	Not annealed . . .	83,700	96,700	143,900	3.3	5.2
		Annealed	82,000	84,400	142,400	5.0	5.3
1.25	1.00	Not annealed . . .	91,700	99,700	147,400	3.1	4.1
		Annealed	82,100	83,700	154,500	6.7	8.0

The results of Hadfield have been confirmed by others, notably Baker,¹ Guillet, and Paglianti. Guillet pointed out the low resistance to impact of silicon steel, a quality which is not indicated by the usual tensile test. The appearance of a small amount of free carbon further lowers the impact strength. This point is not without importance, even though most of the high-tensile silicon steel is used for the manufacture of springs where elasticity and resiliency are ^{here is always} t

¹ *Journ. Iron and S.*

the liability of metallurgists recommending and of engineers using, silicon steels on the basis of a satisfactory combination of high elastic limit and elongation, for purposes which require a considerable degree of notch toughness. In such cases silicon, or silico-manganese steel, should give way to nickel, chrome-nickel, or chrome-vanadium steel. Guillet also noted the marked weakness of silicon steel when broken in a direction transverse to the direction of working.

The effect of quenching pearlitic silicon steel was found by Guillet to be more intensive than quenching the corresponding carbon steels. As an example he cited the heat treatment of spring steels. The types used in France are given as follows: Type 1, carbon 0.45–0.50; silicon 1.50–1.20; Type 2, carbon 0.65–0.70; silicon 0.90–0.80. The properties of Type 1 are given in the following table.

TABLE 95.—MECHANICAL PROPERTIES OF SILICON SPRING STEEL. GUILLET

	Elastic limit, lbs. per sq. in.	Tensile strength, lbs. per sq. in.	Elongation, per cent.
Forged.....	65,400–72,500	106,600–120,900	14–18
Quenched from 900°C.	213,350	213,350	2–0
Quenched in water and tempered.....	142,200–170,600	170,600–192,000	12–5

Resistance to impact varied from 7 to 3 kgm. for the third state, using longitudinal test bars, which is fairly high considering the very great strength. Concerning the properties of 1 per cent. to 1.5 per cent. silicon steel, Paglianti¹ has shown that even the mild or low-carbon steels in the heat treated condition show low impact numbers (Charpy test).

Some of the properties of heat treated “silico-manganese” steel, as obtained by the Bureau of Research of the Midvale Steel Company, are reproduced in Table 96.

The increase in grain size due to the addition of silicon is quite pronounced, and depends upon the conditions of strain of the material, upon the amount and kind of mechanical working of the material, and upon the annealing time and temperature. The grain size cannot be altered except by fairly severe mechani-

work has been considered in Chap. V under the effect of properties of steel.

cal working. The grain size has a considerable effect upon the magnetic properties and will be considered later.¹

TABLE 96.—MECHANICAL PROPERTIES OF SILICO-MANGANESE STEEL

Composition: C, 0.52, Mn, 0.50; Si, 2.225.

Treatment	Properties				
	Tensile strength, lbs. per sq. in.	Yield point, lbs. per sq. in.	Elongation, per cent.	R. A., per cent.	Scler. hardness
Annealed.....	104,000	65,000	26.0	46.0	
1600°F. ½ hr. oil; drawn 3 hr. 600°F.....	304,000	297,500	2.0	1.9	75
1600°F. ½ hr. oil; drawn 3 hr. 800°F.....	240,500	190,000	7.7	29.2	66
1700°F. ½ hr. oil; drawn 3 hr. 600°F.....	323,500	283,500	3.2	12.6	75
1700°F. ½ hr. oil; drawn 3 hr. 800°F.....	245,000	200,000	9.2	28.5	65

Composition: C, 0.35; Mn, 0.52; Si, 2.10.

Annealed.....	94,000	60,000	28.0	52.8	
1600°F. ½ hr. oil; drawn 3 hr. 400°F.....	170,000	148,000	2.0	5.8	51
1600°F. ½ hr. oil; drawn 3 hr. 800°F.....	145,500	100,000	13.5	40.0	52
1700°F. ½ hr. oil; drawn 3 hr. 400°F.....	242,500	232,500	2.0	4.3	64
1700°F. ½ hr. oil; drawn 3 hr. 800°F.....	187,500	130,000	8.7	24.1	55

Electrical and Magnetic Properties.—Silicon has quite a effect on the electrical resistance of iron as is shown by the figure in Table 97.²

TABLE 97.—ELECTRICAL RESISTANCE OF SPECIAL IRON ALLOYS

Metal added	Resistance increases
3 per cent. of Tungsten,	to about 17, or by 2 microhms.
3 per cent. of Nickel,	to about 21, or by 6 microhms.
3 per cent. of Chromium,	to about 24, or by 9 microhms.
3 per cent. of Manganese,	to about 30, or by 15 microhms.
3 per cent. of Silicon,	to about 45, or by 30 microhms.
3 per cent. of Aluminum,	to about 48, or by 33 microhms.

The specific resistance of iron containing approximately the same amounts of impurities as are present in the alloys tested, is 15 microhms per cubic centimeter at room temperature. The table shows the specific resistivities of 3 per cent. alloys. The addition of silicon was found to reduce the coercive force and retentivity (therefore the hysteresis) to nearly one-half of that of

¹ RUDER, *Trans. Amer. Inst. Min. Eng.*, 1913, Vol. 47, p. 569.² BARRETT, BROWN and HADFIELD.

the standard iron rod. The permeability was also higher than that of iron for magnetizing forces below saturation.

These results have been summarized by Baker¹ and are here reproduced in Table 98.

TABLE 98.—MAGNETIC PROPERTIES OF SILICON STEEL

Per cent. Si	Maximum induction, H = 20	Permeability for H = 4	Retentivity	Coercive force	Energy dissipated for complete cycle, ergs per c.c.
0.02	16,000	2325	8375	1.8	10,550
1.02	16,200	2562	8000	1.7	8,798
2.90	15,500	2750	7325	1.5	8,081
4.89	14,750	2665	7200	1.2	6,110
7.47	14,000	2937	9000	1.0	5,613

Greater amounts of silicon lower the magnetic attraction of the iron-silicon alloys still further. The curve representing the variation of the magnetism with silicon content shows breaks at compositions corresponding to Fe_2Si , FeSi and FeSi_2 .²

The beneficial effect on the magnetic properties of iron, secured by the addition of silicon, is brought out by the work of Kolben,³ from which the following figures are taken.

Silicon per cent.	0.02	1.07	2.28	3.25	3.5
T. S. in tons per sq. in.	19.5	22.3	30.0	38.7
Elongation per cent., l = 10d .	11	7.5	6	3.5
Elec. resist. ohms (1m. \times 1mm. ²)	0.118	0.287	0.355	0.50	0.505
Incr. of resist. per 100°C. rise of temperature, per cent.	41	19	14	7.5	5
Incr. resist. (coeff. of hysteresis)	0.0015	0.0014	0.001	0.0009	0.0009
Hysteresis, watts per kg.	2.5	2.2	1.65	1.45	1.45
Eddy currents, watts per kg.	1.3	0.8	0.7	0.6	0.4
Total losses, watts per kg.	3.8	3.0	2.35	2.05	1.85
B for H = 140.	17,600	17,300	17,000	16,700	16,400

Material from the Bismarck Hütte; carbon probably 0.10 per cent.

These figures show that considerable can be expected from low-carbon silicon steel as a medium for transforming electrical

¹ *Loc. cit.* p. 327. See also OTTO, *Ber. physik. Gesell.* 1910, p. 240; and GUMMICH, *Zeit. Elektrochem.*, Vol. 15, p. 597.

² JOUVE, *Compt. Rend.*, 1902, Vol. 134, p. 244; *Journ. Iron and Steel Inst.*, 1908, No. 2, p. 310.

³ *Schweiz. Elektrotechn. Zeit.*, 1909, Vol. 6, p. 201; *Engineering*, 1909, Vol. 87, p. 732.

energy, and it is on account of the low core losses (hysteresis and eddy currents) and high permeability that they are so extensively used in the electrical industries and particularly in the manufacture of transformers. Silicon steel sheets are hard and increasingly difficult to stamp as the silicon increases so that in practice an economic balance is struck between the magnetic properties on the one hand and the mechanical properties and steel costs on the other, to arrive at the correct silicon content to give the maximum transformer efficiency commensurate with a reasonable cost of manufacture. Three per cent. is about the maximum amount of silicon which is used because the alloys become brittle and hard when more than this amount is added.

Not the least important effect of silicon in transformer steel is the conversion of Fe_3C into the less harmful form of graphite, although if the carbon is low the silicon present may be too low to accomplish this. Thus 3 per cent. silicon is too low to graphitize the cementite in low-carbon steel. The annealing temperature must be high enough to decompose the Fe_3C and yet not so high that the carbon passes into solution.¹

In technical practice it is known that the grain size has an important effect on the magnetic properties, and in general an increase in the grain size increases the eddy current losses and the permeability, at least in low and medium fields, and decreases the hysteresis. Cases have been cited where, for constant resistivity and thickness of the laminations, the eddy current losses have been doubled with increase in grain size.²

Further experimentation on the magnetic and electrical properties of silicon steel by Yensen³ seems to show that the effect of silicon is both direct and indirect. Yensen pointed out that "Silicon, like boron, has a double effect on iron; part of it combines with the iron and remains in solid solution throughout the cooling of the alloy while a smaller part reduces the iron oxide present." The magnetic properties showed considerable variation for silicon contents below 1 per cent. although the electrical resistance increased very uniformly. Above 1 per cent. silicon

¹ CHARPY and CORNU, *Compt. Rend.*, 1913, Vol. 156, p. 1616; see also GUMBLICH and GOERENS, *Trans. Faraday Soc.*, 1912, Vol. 8, p. 98.

² RUDER, The Role of Silicon in Alloy Steels, *Proc. A. S. T. M.*, 1917, Vol. 17, Pt. II, p. 15.

³ *Bulletin No. 83, Engineering Experiment Station, University of Illinois*, Nov. 22, 1915.

the properties varied with greater uniformity and the increase in permeability and decrease in hysteresis losses are well brought out. The irregularity which is noted in the alloys containing from 0 to 0.5 per cent. silicon, which were considerable, were not satisfactorily accounted for.

Burgess and Aston,¹ experimenting with electrolytic iron, did not find any general improvement in permeability by the addition of silicon, and the improvement by heat treatment was not as marked as in commercial samples. Evidently the effect of silicon is more pronounced in the presence of impurities.

Chemical Behavior.—Iron silicon alloys are now well known to be highly resistant to the action of acids, and for this reason they are extensively used in the chemical industries. Hadfield, in his original work, brought out the effect of small amounts of silicon in increasing the resistance to dissolution in 50 per cent. sulphuric acid, while Jouve² has considered the whole subject in detail. His tests were conducted on small samples as well as on large vats weighing two tons. He pointed out that in order to secure true resistance to corrosion alloys containing at least 20 per cent. silicon (Fe_2Si) must be used. Commercial alloys, such as Duriron, contain about 14 per cent. silicon and 1 per cent. carbon.

Uses.—The silicon steels are practically limited to three fields. Steels containing from 0.40 to 0.60 per cent. carbon and 1 to 2 per cent. silicon, known as silico-manganese steels, are used for springs and to some extent for gears and in transmission lines. The low cost of these steels and the high elastic limit which can be produced by suitable heat treatment combine to make them very serviceable, although their "great sensitiveness to heat treatment and feeble resistance to shock limits their field of usefulness" (Bullens). The possibility of using silicon steel for compressed air flasks has been suggested by Bisset³ who points out that as compared with high carbon steels, high tensile strength can be obtained without sacrificing the ductility and impact resistance. Low carbon silicon steel, containing up to 3.5 per cent. silicon, is extensively used in the construction of dynamos and transformers, on account of the low hysteresis and eddy current losses. Its use has also been suggested for telephone service, inasmuch as sounds of

¹ *Met. and Chemical Eng.*, 1910, Vol. 8, p. 131.

² *Loc. cit.*

³ *Iron Age*, 1910, Vol. 86, p. 442.

the same intensity can be produced with a considerable saving of electrical energy.¹ Ferrosilicons containing higher amounts of carbon are extensively used in the chemical industry as containers for sulphuric acid and for other uses where resistance to chemical action is required.

ALUMINUM STEEL

Metallic aluminum is now extensively added to steel, not to form a constituent of steel nor to alter its properties, but to moderate the harmful effects of oxygen and other gases. This use of aluminum is known as "deoxidation" or "degasification." As an alloy-forming constituent in steel, aluminum has been quite thoroughly investigated and it has long since been found to possess little merit in this field. The influence of aluminum on iron, steel and cast iron was early considered by Keep,² and in 1890 Hadfield reported very fully on the properties of aluminum steel.³

The constitution of the iron-aluminum alloys was reported on by Guillet⁴ who found a compound Fe_2Al_3 . Gwyer⁵ found a compound FeAl_2 which was soluble in iron in all proportions but not in aluminum. He also noted that aluminum lowers the melting point of iron to 1150°C . at 50 per cent. aluminum. Osmond determined the cooling curve of a 5 per cent. aluminum steel and found no heat effect.⁶ Gwyer found the magnetic transformation up to 20 per cent. aluminum, but reported that 1 per cent. aluminum eliminated the A_3 point (?) According to Guillet's work the A_1 point is present in aluminum steel, contrary to the work of Osmond. Arnold, in 1894, reported that only the A_{r2} point occurs and not the A_{r3} , in low carbon steel.

¹ *Elec. Rev. West. Elec.*, Vol. 58, p. 456.

² See for example, *Journ. Iron and Steel Inst.*, 1890, No. 1, p. 112. In a discussion of this paper, MR. JAMES RILEY gave the influence of aluminum on cast, rolled and annealed steel and brought out that it is of very doubtful advantage, even with less than 0.5 per cent., except to increase the fluidity, and that it increases the grain size of cast steel. HADFIELD reported that 5 per cent. aluminum has a very slight lowering effect on the melting point of iron.

³ *Journ. Iron and Steel Inst.*, 1890, No. 2, p. 161.

⁴ *Compt. Rend.*, 1902, Vol. 132, p. 236.

⁵ *Zeit. anorg. Chem.*, 1903, p. 113.

⁶ *Journ. Iron* . . . 1, p. 38.

The microstructure and mechanical properties were reported on by Guillet,¹ who noted that steels containing up to about 3 per cent. aluminum were pearlitic.

Barrett, Brown and Hadfield found the effect of aluminum on the magnetic properties of iron to be similar to that of silicon, and, accordingly, the low-carbon alloys are at times used in transformer and dynamo construction.² The electrical conductivity of aluminum steels, forged and quenched, was studied by Portevin.³ He found that the conductivity decreased rapidly with addition of aluminum but much less so by quenching.

TERNARY TOOL AND CUTLERY STEEL

The elements which are added to steel for tool and cutlery purposes are those lying to the left of iron and manganese in the periodic system. These elements, such as chromium, tungsten, molybdenum, vanadium, etc., have a special affinity for carbon, or the carbide Fe_3C and their principal effect in steel is to produce great cutting hardness in combination with a greater degree of toughness than can be secured with carbon steel. Historically, these steels are older than the construction steels and probably so because the tool steel industry was well developed considerably prior to the extensive expansion in engineering practice which called forth the special construction steels.

CHROMIUM STEEL

The early history of chromium steel has been given by Hadfield⁴ in his report of the first systematic investigation of these alloys. The element chromium was discovered by Vauquelin in 1787. He separated the metal from red lead chromate and determined most of the properties. Faraday produced an alloy of iron and chromium as early as 1820, while in 1821 Berthier⁵ contributed the results of his experiments on chromium steel and the production of a 17 per cent. ferrochromium with which

¹ *Compt. Rend.*, 1905, Vol. 141, p. 35; *Alliages Metalliques*, p. 364.

² The magnetic properties of aluminum steel were also studied by RICHARDSON, *Phil. Mag.*, 1900, Vol. 49, p. 121; 1901, Vol. 50, p. 296; 1901, Vol. 51, p. 601.

³ *Rev. de Met.*, 1909, Vol. 6, p. 1335.

⁴ *Journ. Iron and Steel Inst.*, 1892, No. 2, p. 49.

⁵ *Annal. de Chimie*, 1821, Vol. 17.

steels containing 1 to $1\frac{1}{2}$ per cent. chromium were made. Berthier noted among other things the great hardness, brittleness, infusibility and resistance to the action of strong acids exhibited by these alloys, which in all probability contained considerable carbon. After Faraday,¹ perhaps the first production of chromium steel on a commercial basis was by Bauer of Brooklyn, New York, who took out a patent on the manufacture of chromium steel in August, 1865. Soon thereafter chromium steel was produced in France by Brustlein² and then in Germany and elsewhere, whereupon it became a common article of commerce although the uses of chromium steel were then and are now somewhat limited.

Two other important reports on chromium steel, prior to that of Hadfield, were those of Kern³ and of Hart and Calisch.⁴

Chromium steel is made in the open hearth, crucible, or electric furnace. When high carbon ferrochrome is used, it is difficult to produce homogeneous ingots on account of the infusibility of the chromium carbide and the slowness with which it dissolves and diffuses into the steel bath. For this reason, low carbon ferrochrome, as produced in the electric furnace, is largely used in the manufacture of chromium steel. Hadfield found it necessary to add aluminum or silicon to produce sound ingots but that this was less so with the higher chromium contents, which were higher in carbon. The forgeability of chromium steel is equal to that of ordinary carbon steel although, on account of its low thermal conductivity, greater care must be exercised during heating. Hadfield showed that chromium is not favorable to welding.

Fusion Curves.—Data concerning the melting and freezing points of chromium steel are very meager. The freezing point determinations of Treitschke and Tammann⁵ were quite irregular and varied nearly 200°C. above and below the mean of the freezing points of iron and chromium. An important point here is that the freezing point of the 10 per cent. alloy was found to be nearly 100° lower than the freezing point of iron while that of the 20 per cent. alloy was approximately the same.

¹ *Philosophical Trans.*, 1833, p. 253.

² *Journ. Iron and Steel Inst.*, 1886, No. 2, p. 770.

³ *Journ. Iron and Steel Inst.*, 1887, No. 1, p. 231.

⁴ *Journ. Stevens Inst. Tech.*, 1892, Vol. 9, No. 1.

⁵ *Zeit. anorg. Chemie*, 1907, Vol. 55, p. 402.

Various irregularities were noted in the behavior of these alloys which pointed toward the gradual formation of a compound of iron and chromium, such that the system behaved as a pseudo-ternary system. Guertler observes in his book, relative to this compound, that it does not exist as a separate phase but as a more or less dissociated compound dissolved in the alloys of iron and chromium—illustrating again the necessity of distinguishing between molecules and phases. Treitschke and Tammann point out that iron and chromium as such are not miscible in the solid state in all proportions, but that it is necessary, first of all, to form the compound which is then miscible with both iron and chromium in all proportions. This compound is supposed to break down at lower temperatures so that homogeneous alloys on remelting become heterogeneous mixtures of two different phases. Guertler points this out as an interesting case of the influence exerted on heterogeneous equilibria by changes in the homogeneous equilibrium of a single phase.

These results have been verified with a series of low carbon, iron-chromium alloys made by the Goldschmidt process.¹ In this series it may well be assumed that the chromium compound (probably Cr_2Fe) forms at the high temperatures of the aluminothermic process to explain the behavior of the alloys in the neighborhood of 65 or 70 per cent. chromium.

The irregularities are held by Jancke to be due to aluminum contained in the alloys inasmuch as he found an eutectic at 75 per cent. chromium and 1320°C . The constituents of the eutectic were found to be solid solutions containing 55 per cent. and 85 per cent. chromium respectively.²

Critical points.—The results of Osmond's work are given in Table 99, about which he remarks as follows.

The beginning of Ar_3 is lowered by the increase in carbon, but the point would be lower if there were no chromium present. The action of Ar_2 is not noticeable, while the position of Ar_1 is in all cases somewhat higher than it would be if chromium were absent.

¹ MONNARTZ, *Metallurgie*, 1911, Vol. 8, p. 161.

² *Zeit. Elektrochem.*, 1917, Vol. 23, p. 49.

TABLE 99.—CRITICAL POINTS OF CHROMIUM STEEL

	Ar ₃			Ar ₂			Ar ₁				
	Begin about	Max.	End about	Begin	Max.	End	Begin	Max.	End		
1176B	865	845-835	825	755	740-730	720	680	680-670	660		
1176C	835	810-800	785	740	720-710	700	690	680-670	660		
1176E	825	805-795	785	740	720-710	700	700	690-680	670		
1176F				780	769-750	725	700	700-690	680		
1176J				780	740	720	Recalescence at 682-692				
				incomplete							
1176L							Recalescence at 684-704				

Composition						
	C	Si	S	P	Mn	Cr
1176B	0.16	0.07	0.10	0.04	0.18	0.29
1176C	0.15	0.10	0.09	0.04	0.21	0.48
1176E	0.12	0.08	0.10	0.04	0.018	0.84
1176F	0.27	0.12	0.13	0.04	0.21	1.18
1176J	0.77	0.50	0.11	0.04	0.71	5.19
1176L	0.71	0.36	0.10	0.03	0.25	9.18

The raising of the critical point of chromium steel by the addition of chromium was later confirmed by the work of Carpenter¹ whose results, obtained by cooling from about 900°C., follow.

Carbon, per cent.	Chromium, per cent.	Ar, °C.	Ac, °C.
0.54	1.12	729	759
0.27	3.24	738	
0.09	9.55	776	

The alloy with 0.77 per cent. carbon, 5.19 per cent. chromium and 0.61 per cent. manganese (Osmond) showed a marked lowering of the critical points on increasing the rate of cooling, while cooling in nine seconds from 920°C. to 300°C. suppressed the point entirely and produced the same effect as quenching does on carbon steel. In the same manner, increasing the initial temperature from which cooling commenced produced a marked

¹ *Journ. Iron and Steel Inst.*, 1905, No. 1, p. 443.

lowering and weakening of the critical point so that the steel became much harder than on cooling from lower temperatures. Osmond explained this as being due to the solution in the iron of a compound of iron, carbon and chromium at the high temperature which did not have time to aggregate on cooling.¹ Just recently Murakami has explained that the carbide Cr_4C dissociates into Cr_3C_2 and Cr on heating above Ac_1 , and that the higher the temperature, the more the dissociation proceeds; the chromium dissolves in the iron. On cooling, the reformation of Cr_4C takes place slowly with the result that the transformation on cooling is lowered and easily suppressed, and the steel is hardened. The hardness is due to the solution of Cr_3C_2 in the chromiferous iron. If the rate of cooling is very slow, the carbide Cr_4C again forms and the transformations occur at their normal temperatures.²

The action of chromium in conferring air- or self-hardening properties on steel was also considered by Carpenter who found that steels containing smaller amounts of manganese and silicon are practically not affected by raising the initial temperature, inasmuch as only a slight lowering of the critical points was found.

This apparent discrepancy was explained later by Edwards, Greenwood and Kikkawa³ who found that the suppression of the critical points depends upon the rate of cooling and that the "critical cooling velocity" drops as the heating temperature is raised. As soon as the critical cooling velocity is exceeded, martensite makes its appearance in the microstructure and the steel becomes hard. They used a steel with 0.63 per cent. carbon, 0.07 per cent. silicon, 0.17 per cent. manganese and 6.15 per cent. chromium.

One of the effects of adding chromium is that the A_1 point is raised above the A_2 point. About 3 per cent. chromium is required to do this, according to Moore,⁴ although McWilliams and Barnes found the same thing in their 2 per cent. chromium steels.⁵ In this way Ac_1 rises from 746°C . in the steel containing 0.25 per cent. chromium to 821°C . in the steel containing 6.417 per

¹ OSMOND further commented on the great hysteresis of these steels and their possible use as permanent magnets.

² MURAKAMI *Sci. Rep. Tôhoku*, 1918, Vol. 7, p. 217. See also *Journ. Iron and Steel Inst.*, 1919, No. 2, p. 445.

³ *Journ. Iron and Steel Inst.*, 1916, No. 1, p. 114.

⁴ *Journ. Iron and Steel Inst.*, 1910, No. 1, p. 268.

⁵ *Ibid.*, p. 246.

cent. chromium. The curves in Fig. 126 taken from the work of Moore illustrate this point. That A_1 comes above A_2 can be shown by means of the magnetic transformation which occurs at A_2 (Moore). In the light of the laws of heterogeneous equilibria, there is nothing complicated about this effect, because all it means is that the iron loses its magnetism before the equilibrium —austenite, ferrite, cementite— is passed through.¹ The magnetic transformation seems to occur at 777°C. on both heating and cooling and is little affected by the maximum heating tem-

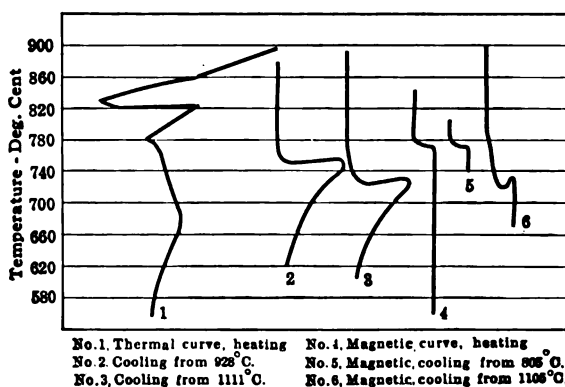


FIG. 126.—Thermal and magnetic critical points of 2 per cent. chromium steel. (Moore.)

perature although heating to 1105°C. shifts the end of the transformation on cooling to somewhat lower temperatures.

The critical point determinations of McWilliams and Barnes on their 2 per cent. chromium series are given in Table 100.

We see that wherever free iron is present, the magnetic transformation takes place about at 760° both on heating and on cooling. Ac_1 shows a slight tendency to drop as the carbon increases but it occurs at essentially the same temperature irrespective of the carbon content. Ac_3 shifts to lower temperatures with increase in carbon, the same as in carbon steel. On cooling,

¹ The author has noted the same thing in high speed steel in his laboratory. If a specimen of high speed steel is heated to above its magnetic transformation but below its structural transformation, the magnetic change occurs at the same temperature on cooling that it does on heating. If the heating is carried above the A_1 point, on cooling there is no free iron at the normal A_2 point and the steel does not become magnetic until the Ar_1 change is passed through at a considerably lower temperature.

TABLE 100.—CRITICAL POINTS OF TWO PER CENT. CHROMIUM STEELS

Mark	Composition			Ac ₂ , °C.	Ac ₁ , °C.	Ac ₃ , °C.	Ar ₃ , °C.	Ar ₂ , °C.	Ar ₁ , °C.
	C	Cr	Mn						
1154	0.20	1.98	0.12	765	791	7822	785	765	732
1153	0.25	1.99	0.23	759	789	7810	758		731
1152	0.32	1.98	0.23	753	785		748		733
1157	0.50	1.99	0.24	759	778		721		
1168	0.65	2.07	0.22	783			718		
1155	0.85	2.00	0.24	777			714		

The heating curves published in the paper apparently have an Ac₂ point at about 760° for No. 1168 and a less pronounced one at the same temperature in No. 1155 but which is probably merged with the beginning of Ac₁.

if the carbon content is low enough to cause the separation of any iron above 760°, Ar₂ would come above Ar₁ and there should be a separate magnetic transformation point. In higher carbon steels the Ar₂ point is merged with the Ar₁ point which auto-

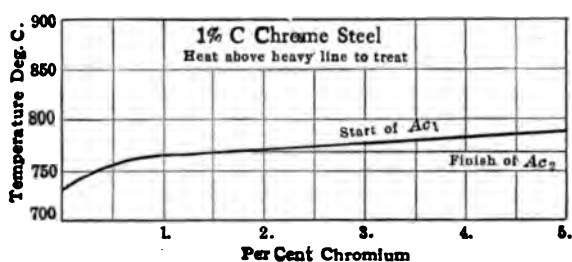


FIG. 127.—Critical points of chromium steel with 1 per cent. carbon. (Midvale Steel Co.)

matically lowers the Ar₂ point to Ar₁. This is in accordance with the present ideas on the A₂ transformation point as affected by temperature and phase phenomena.

The critical points of 1 per cent. carbon steels with increasing amounts of chromium are given in Fig. 127. In a steel with 1.50 per cent. carbon and 15 per cent. chromium the Ac₁ transformation took place between 724°C. and 730°C., while Ac₁ occurred at 735 to 715°C. (Scott).

Microstructure.—In his original work cited above, Osmond concluded that chromium may exist in steel in at least three states, either separately or simultaneously; (1) in the state

of dissolved chromium; (2) in the state of a compound of chromium, iron and carbon, in the form of isolated globules; or (3) in the same condition as (2) in the form of a solidified solution. Pure chromium dissolved in pure iron appeared to have no physico-chemical action, but it did appear to have a decided influence on the crystallization of the iron, which was especially important from the point of view of mechanical properties. In this way chromium interfered with the crystallization of iron and diminished the grain size.¹

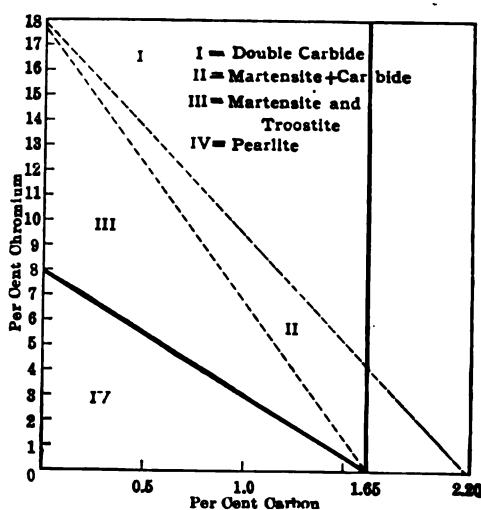


FIG. 128.—Microstructure of forged chromium steel. (Guillet.)

The microstructure of the chromium steels has been further considered by Guillet who has given us the results in Table 101 and Fig. 128.² These results were obtained from the examination of forged and slowly cooled steels.

The effect of the first additions of chromium is to make the steel finer grained and to disseminate the carbide. The effect of chromium in making steel fine grained can be seen from Fig. 129 which shows a steel with 0.80 per cent. carbon, and 1.73 per cent. chromium after heating for six hours at 1040°C. and cooling slowly to room temperature. The structure is very fine grained pearlite. With further additions of chromium, the steels re-

¹ See also BRUSTLEIN, *Journ. Iron and Steel Inst.*, 1886, No. 2, p. 770.

² *Etude Industrielle des Alliages Metalliques*, p. 326. *Rev. de Met.*, 1904, Vol. 1, p. 155.

TABLE 101.—MICROSTRUCTURE OF CHROMIUM STEEL

Class	Microstructures	Steels with 0.20 per cent. C	Steels with 0.80 per cent. C
1	Pearlite, per cent. Cr.....	0 to 7	0 to 3
2	Martensite and troostite, per cent. Cr.....	7 to 15	3 to 10
3	Special constituent and Marten- site, per cent. Cr.....	15 to 20	10 to 18
4	Special constituent, per cent. Cr.	20	18

semble quenched carbon steels and contain martensite and troostite. This, of course, does not mean that the "air-hardened"



×400

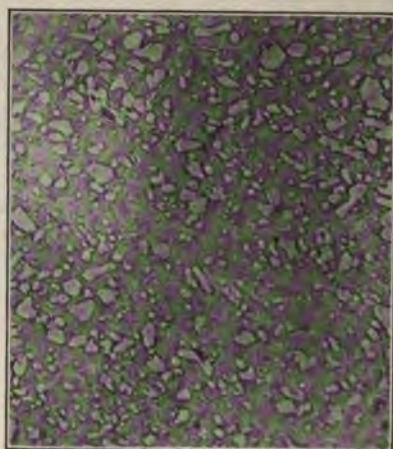
FIG. 129.—Microstructure of chromium steel containing 0.80 per cent. carbon and 1.73 per cent. chromium, drastically annealed.

condition is the stable condition of these steels because it is well known that rates of cooling which leave carbon steel soft may act as a quench for alloy steels and produce unstable structures. Portevin has shown that a steel with 0.12 per cent. carbon and 17.38 per cent. chromium, when slowly cooled from 1300°C., is soft and comparable to slowly cooled carbon steels.¹

The third field is supposed to represent a transition zone between the martensitic steels and the carbide steels. These results demonstrate that a certain amount of chromium, depending upon the carbon content, can be added to steel without materially

¹ *Compt. Rend.*, 1911, Vol. 153, p. 64.

affecting the microconstituents, the principal effect being what might be termed a sluggardizing effect on the crystallization of both the ferrite and the pearlite. The addition of more chromium produces the structure of hardened steels. On further increasing the chromium, the martensite begins to disappear, and more or less malformed polyhedra enter, which contain traces of fine-grained martensite, in their interiors. This can be observed by etching with hydrochloric acid or with potassium bisulphate. Increasing the chromium still higher, up to 18 per cent. and above, gives a polyhedral structure containing the carbide as small white crystals but exhibiting no martensitic



×800

FIG. 130.—The carbide in chromium steel.

structure. The steels with 0.8 per cent. carbon were pearlitic up to about 3 per cent. chromium. From 3 to 9 per cent. chromium a dark constituent (on etching), resembling troostite was present. A further increase of the chromium produced martensite as before, until with the final disappearance of the martensite the steels showed a polyhedral structure with white structureless crystals, the carbide. The appearance of this carbide can be seen in Fig. 130.

Guillet points out that although this constituent presents different characteristics than cementite of ordinary steel, it must be carbide because it can be produced by cementing a pearlitic or a martensitic steel. Guillet remarks of the third

zone of martensite and the double carbide, that it is more a transition zone and less sharply defined than the others.

The position of the pearlite point in the pearlitic chromium steels is not given by Guillet, but McWilliam and Barnes point out that in their series of steels containing 2 per cent. chromium it undoubtedly lies between 0.65 and 0.85 per cent. carbon. Here, again, the exact position of the pearlite point would be difficult to locate on account of the lack of sharp distinction between the hyper and hypo-eutectoid steels.

The Carbide in Chromium Steel.—The question of the distribution of the carbon in chromium steel is one of considerable importance, not alone in connection with the properties and behavior of chromium steel but also on account of its bearing on high speed steel and its heat treatment. This has been dealt with by Arnold and Rhead in a very important paper on the subject.¹ They review, first of all, the previous work on the carbides of chromium and point out that two carbides of chromium were known to exist, Cr_3C_2 and Cr_4C .² The alloys made contained about 0.85 per cent. carbon, 0.65 to 23.70 per cent. chromium and small amounts of impurities. The bars were drastically annealed to precipitate all of the carbon as carbide and tested for mechanical properties. The carbide was separated electrolytically and analyzed for iron, chromium and carbon. The results showed that chromium replaces iron in the carbide as the chromium increases in amount up to about 10 per cent. chromium, at which point the carbide contains about 63 per cent. chromium and 8 per cent. carbon. The carbides were said to be solutions of Fe_3C , Cr_3C_2 and Cr_4C depending on the amount of chromium in the steel although no distinction was made microscopically between the carbides. Mechanically, the carbide Cr_4C is considerably softer than Cr_3C_2 , which scratches topaz.³ With 15 per cent. chromium, the carbide is a mixture of Fe_3C and Cr_4C . Nearly one-half of the chromium present dissolves in the iron to form chromiferous-ferrite. The microstructure of

¹ *Journ. Iron and Steel Inst.*, 1911, No. 1, p. 249.

² MOISSAN, *The Electric Furnace*, 1904, p. 144. Cr_4C is disputed by RUFF and FOCHR (*Zeit. anorg. Chem.*, 1918, Vol. 104, p. 27), who found Cr_3C_2 , Cr_7C_3 and others but not Cr_4C .

³ That the double carbide of iron and chromium is harder than the simple iron carbide is shown by the work of BOYNTON to which reference has already been made. He showed that pearlite containing 1 per cent. Cr is seven times as hard as pearlite in the common steels.

the drastically annealed steels showed mixtures of chromiferous-ferrite and the double carbide, the latter occurring first in pearlite and then, with more chromium, as isolated globules. This elicited the opinion from Professor Carpenter that Guillet's classification of the microstructure was incorrect and that the martensitic steels had no rightful place in the diagram.

The Heat Treatment and Mechanical Properties of Chromium Steel.—A general survey of the mechanical properties of the chromium steels can be obtained from the work of Hadfield and Guillet. The properties of chromium steel in the usual forged condition, as given by Guillet, are reproduced below.

TABLE 102.—MECHANICAL PROPERTIES OF FORGED CHROMIUM STEEL

Composition		T. S., lbs. per sq. in.	E. L., lbs. per sq. in.	Elong., per cent.	R. A., per cent.	Brinell hardness	Resi- ance shoc.
C	Cr						
0.20	0.7	49,700	32,700	27	75	85
0.20	1.2	78,200	60,000	15	57	130	20
0.20	4.5	85,000	79,000	16	65	160	25
0.20	7.8	213,300	142,200	5	7	365	9
0.20	9.1	204,800	183,000	3	5	350	10
0.20	10.1	197,000	142,200	3	0	385	9
0.20	13.6	125,000	73,000	3	7	270	3
0.20	14.5	142,200	126,000	3	7	240	3
0.20	22.0	92,490	55,470	15	25	170	2
0.20	25.3	79,800	56,900	18	52	185	1
0.20	31.7	79,600	64,000	12	50	160	1
0.80	0.5	154,600	110,000	2	15	320	3
0.80	1.0	184,900	184,000	3	7	330	2
0.80	2.0	197,000	139,000	3	0	360	3
0.80	4.5	187,000	119,400	2	8	295	3
0.80	7.2	177,000	86,000	3	15	375	5
0.80	9.3	135,000	112,000	12	0	385	3
0.80	11.5	190,000	112,000	5	14	325	1
0.80	14.5	170,600	92,400	3	0	475	6
0.80	18.5	180,000	180,000	2	0	380	2
0.80	26.5	85,300	71,000	10	45	175	1
0.80	32.5	96,000	80,000	15	40	195	2

NOTE.—The carbon contents were those aimed at and actually the carbon varies from the percentages given.

The mechanical properties clearly bring out the different kinds of steel represented in Fig. 128. The pearlitic steels have properties analogous to the carbon steels. Chromium increases the tensile strength but decreases the ductility. The martensitic steels are very hard and strong but lacking in ductility and resistance to impact. The hardness of the martensitic steels

does not vary much with either the chromium or the carbon. The martensitic steels containing at the same time the double carbide, are very strong and more fragile than the simple martensitic steels. The polyhedral steels characterized by the double carbide have a low tensile strength and an appreciable amount of ductility but are very weak under impact. They correspond to the polyhedral nickel steels but they are much more fragile.

Work on these steels, in accordance with the use of these steels, has been largely limited to certain compositions. The properties of a graded series of 2 per cent. chromium steels are given in Table 103.¹

TABLE 103.—MECHANICAL PROPERTIES OF CHROMIUM STEEL
McWILLIAMS AND BARNES

Mark	Composition		Yield point, lbs. per sq. in.	Tens. str., lbs. per sq. in.	Elong., on 2 in.	R. A., per cent.	Arnold's stress test
	C	Cr					
1154A	0.20	1.98	35,840	73,920	40.5	77.9	410
1153A	0.25	1.99	35,840	78,400	39.5	73.8	437
1152A	0.32	1.98	32,256	68,096	37.0	70.7	482
1157A	0.50	1.99	28,672	84,224	28.0	55.4	440
1168A	0.65	2.07	71,680	109,400	21.5	62.2	214
1155A	0.85	2.00	42,112	90,000	32.0	63.5	316
800°C. Water and 400°C. Air							
1154Y	0.20	1.98	150,080	153,664	12.5	40.6	96
1153Y	0.25	1.99	175,392	197,568	12.0	42.5	103
1152Y	0.32	1.98	206,080	224,000	9.5	37.0	94
1157Y	0.50	1.99	250,880	255,584	9.0	30.3	88
1168Y	0.65	2.07
1155Y	0.85	2.00
800°C. Water and 550°C. Air							
1154X	0.20	1.98	123,200	129,920	16.0	50.7	144
1553X	0.25	1.99	152,320	161,280	14.5	51.5	99
1152X	0.32	1.98	169,900	178,300	15.0	52.2	141
1157X	0.50	1.99	190,400	200,700	13.0	42.5	111
1168X	0.65	2.07	210,600	216,000	10.0	32.4	74
1155X	0.85	2.00	207,000	214,200	8.5	28.2	65

Annealed chromium steel is not much harder than carbon steel but the effect of quenching on the former is much more intense. This behavior of chromium steel is very valuable in technical practice inasmuch as parts can be machined and then heat treated to be put into the proper condition.

¹ *Journ. Iron and Steel Inst.*, 1910, No. 1, p. 246.

TABLE 104.—PROPERTIES OF 1 PER CENT. CHROMIUM STEEL—THE MID-VALE STEEL COMPANY

Carbon, per cent.	Final quench- ing, °C.	T. S., lbs. per sq. in.	E. L., lbs. per sq. in.	Elongation, per cent.	R. A., per cent.
Drawn at 205°C.					
0.25	835	167,500	Not given	8	35.5
0.40	790	216,500	
0.50	790	238,500		0.5	1.5
Drawn at 315°C.					
0.25	835	169,000	Not given	14.5	47.0
0.40	790	223,000		2.0	4.5
0.50	790	259,000		8.0	15.5
Drawn at 430°C.					
0.25	835	153,000	122,000	11.5	56.0
0.40	790	214,000	185,000	10.5	45.0
0.50	790	230,000	197,000	10.0	41.5
Drawn at 540°C.					
0.25	835	126,000	105,000	16.0	64.0
0.40	790	160,000	137,000	15.5	57.5
0.50	790	176,000	157,000	14.0	51.5
Drawn at 650°C.					
0.25	835	104,000	87,500	20.0	71.5
0.40	790	127,000	110,000	19.5	64.5
0.50	790	133,000	115,000	19.0	62.0
CRITICAL POINTS					
C	Ac ₁ , °C.	Ac ₃ , °C.	Ar ₃ , °C.	Ar ₁ , °C.	
0.25	760	813	763	700	
0.40	705	774	720	704	
0.50	Ac =	765	Ar =	696	

Bars were "fibred" in 1 inch round bars by a high and a low quench and a high draw. Bars were then turned to 0.505 inch. and treated as given in the table.

From the properties of chromium steel, it is apparent that it will be principally used when cutting hardness and resistance to wear are desired. These properties are secured by the formation of the double carbide and its formation of chromiferous martensite which produces a very hard steel. In the forged condition, chromium steel is very hard and for machining must be softened by very thorough annealing. This behavior of chromium steel is indicated by the effect of chromium in intensifying the air hardening ^r steel.

As a consequence of this effect of chromium we have its effect in increasing the efficacy of heat treatment, particularly as applied to the larger sized parts. Such parts made of carbon steel might be satisfactorily treated on the outer layers but the interior would be soft and would lack in grain refinement. With small amounts of chromium added, the hardening effect penetrates to the core. In the same way the necessity for rapid quenching decreases and equally satisfactory results (hardness and grain refinement) can be secured by oil quenching, or even by air cooling.¹ This effect is not due to chromium alone but depends upon the combined action of chromium and carbon. The carbon-free alloys of iron and chromium are not at all hard and difficult to machine, as is generally assumed.²

Two common composition which are used contain 0.5 per cent. chromium and 1.0 to 1.5 per cent. chromium. The former with about 0.7 per cent. carbon to 1.0 per cent. carbon is used for chisels, while other carbons have been used extensively for drills, saw blades, files, etc. The second grade containing about 1 per cent. carbon is used very extensively for ball bearings, conical bearings, in crushing machinery, and for the special uses where very great hardness is required. A very excellent grade of cold rolls is made of steel with about 1 per cent. carbon and 3 per cent. chromium. These steels require very careful handling during heat and mechanical treatment. Another special use of chromium steel is as a non-deforming tool or die steel which contains about 1 per cent. carbon and 17 per cent. chromium.

A study of the chemical behavior of the chromium steels has shown that they possess not alone great cutting hardness, but also resistance to ordinary chemical action. Monnartz,³ who verified and extended the work of Berthier, found that the addition of chromium to iron increased the stability in nitric acid but apparently decreased it in hydrochloric and sulphuric acids. Carbon added to iron-chromium alloys was found to increase the resistance to acids. Accompanying this action is a considerable increase in hardness and brittleness. This behavior is common to tungsten, molybdenum, titanium and vanadium, which likewise increase the stability of steel in acids. The mechanical strength of the carbonless alloys of iron and chromium

¹ GRENET, *Journ. Iron and Steel Inst.*, 1917, No. 1, p. 107.

² MONNARTZ, *Metallurgie*, 1911, Vol. 8, p. 161.

³ *Loc. cit.*

and the superior resistance to corrosion is held to be of considerable technical importance. More recently the use of a steel containing about 14 per cent. chromium and 0.5 to 0.6 per cent. carbon has been patented for cutlery. This steel is known as "stainless steel," and does not tarnish in ordinary service.

Conductivity.—The electrical conductivity of chromium steel, as determined by Hopkinson, is but little less than that of carbon steel with the same carbon content. This would indicate that the chromium is present largely as the carbide and not in solution in the iron.

The thermal conductivity of chromium steel is low so that exceptional care must be taken when heat treating large masses of chromium steel to avoid setting up severe internal strains. Experience in the heat treatment of chromium steel rolls has taught that they must be very carefully heated, as they have been known to explode when heated too rapidly.

The Magnetic Properties.—The great hardness of chromium steel has led to numerous investigations of the magnetic properties, especially the remanent magnetism and stability. It has been shown by Hadfield, Treitschke and Tammann, and others, that iron-chromium-carbon alloys are strongly magnetic even when they contain an appreciable amount of chromium, but that, as would be expected, the magnetism decreases with drop in the iron content.¹

Chromium steel does not make as good a magnet steel as tungsten steel does but during the war when tungsten was so scarce and so high priced, it was used extensively as a substitute. One of the best compositions for this purpose, as developed by Mars, contains 1.05 per cent. carbon and 1.62 per cent. chromium.²

TUNGSTEN STEEL

Tungsten occupies a position in the periodic system on the same side of iron as chromium, from which we would expect it to have somewhat the same effect in steel as chromium, which is true to fact. Tungsten acts as a hardening agent and also increases the resistance of the steel to the tempering action of

¹ See also CURIE (*Bulletin de la Soc. d'Encourag.*, 1898, p. 54) who found that 2.5 to 3.5 per cent. chromium increased the coercive force and the remanent magnetism.

² *Stahl u. Eisen*, 1909, Vol. 29, p. 1771.

the heat generated during cutting. On this account, the tungsten steels are used for tools requiring cutting hardness. One of the leading characteristics of tungsten steel is the extremely fine grain which it acquires when properly heat-treated, and which, with the hardening effect of the tungsten, gives steels which combine hardness and toughness to a remarkable degree. The fine grained or porcellanic fracture of the heat treated steel is used as an indication that the treatment was properly done.

The history of the discovery of tungsten steel has been fairly controversial and will not be entered into here, but it is probably fair to state that the first tungsten steels were produced in Austria from Styrian ores and tests were carried out as early as 1856 at the Royal Polytechnic Institute at Vienna. These steels were all low in tungsten and the first commercial production of tungsten steel in the form in which it is now used, is due to Mushet of England inasmuch as he was first to bring out the remarkable effect of the larger amounts of tungsten.

One of the early treatises on tungsten steel is that of Heppe in 1886¹ in which he discusses the various uses, actual and possible, of tungsten steel. He recommends the following compositions for the different purposes: For tools and cutlery, shears, knives, etc., a tungsten content of 7.5 per cent.; for locomotive tires, a tungsten content of 2.5 to 5 per cent.; and for axles, a tungsten content of 0.5 to 1.5 per cent. Hadfield has also given a thorough account of the early history and use not only of tungsten steel but of tungsten ore, ferro-tungsten and metallic tungsten.² In this paper Hadfield contributes the results of his own extensive investigations of tungsten steel; these tests include the effect of heat-treatment, tests of the mechanical properties, welding tests, corrosion tests, and magnetic tests. This treatise has been freely consulted in the preparation of the present text and the results will be referred to at greater length in the following. Hadfield's tests were conducted on steels which varied in composition from 0.13 per cent. carbon and 0.10 per cent. tungsten up to 0.89 per cent. carbon and 16.18 per cent. tungsten.

The Constitution of Tungsten Steel.—The binary alloys of tungsten and iron, mainly those rich in iron, have been investigated to quite an extent in the past but, in spite of this fact, their constitution is not at all known at the present time. This is

¹ HEPPE, *Stahl u. Eisen*, September, 1886.

² HADFIELD, *Journ. Iron and Steel Inst.*, 1903, No. 2, p. 14.

probably largely due to the experimental difficulties of preparing alloys with the higher tungsten contents which have such high melting points. From the work which has been done, it is apparent that iron and tungsten form both solid solutions and intermediate phases and furthermore that conditions of stable equilibrium form with extreme sluggishness. In this way the iron-tungsten alloys behave similarly to the iron-chromium and iron-molybdenum alloys.¹

Turning now to the iron-rich alloys of iron and tungsten we find that the first additions of tungsten lower the melting point of iron;² in fact 10 per cent. of tungsten is said to lower the melting point by 75 degrees Centigrade, an effect which is equivalent to that produced by 0.7 per cent. of carbon.³ We find also that there has been no systematic investigation of the critical points of tungsten steel, the work which has been done having been limited to certain selected steels.

The melting points of various tungsten steels as determined by Boehler are given in Table 105.

TABLE 105.—MELTING POINTS OF TUNGSTEN STEELS. BOEHLER

No.	Composition				Melting point, °C.	Recalcescence, °C.
	C	Si	Mn	W		
1	0.85	0.14	0.08	0.46	1476	
2	0.86	0.08	0.09	1.93	1472	
3	0.81	0.09	0.14	1.85	1474	
4	0.66	0.03	0.04	3.11	1488	
5	0.68	0.09	0.12	7.63	failed	
6	0.93	0.18	0.18	1.03	1465	
7	0.82	0.11	0.17	3.95	1470	585
8	0.75	0.13	0.21	7.23	1439	540
9	1.16	0.15	0.21	7.05	1387	
10	1.14	0.23	0.57	14.12	1318	
11	0.95	0.09	0.13	0.64	1459	710
12	0.85	0.12	0.21	7.78	1421	540
13	1.02	0.26	0.24	10.40	1388	
14	0.98	0.05	0.45	16.84	1348	

Harkort reported that the $\alpha = \beta$ transformation was unaffected

¹ See GUERTLER, "Metallographie," Vol. 1, Pt. 1, p. 380, who discusses the work which has been done on the iron-tungsten alloys up to about 1910.

² HARKORT, *Metallurgie*, 1907, Vol. 4, p. 617.

³ BOEHLER, "Tungsten and High Speed Steel," 1904.

by tungsten but that the $\beta = \gamma$ transformation was raised. Osmond,¹ on the other hand, reported that the $\beta = \gamma$ transformation was not changed by tungsten but that the $\alpha = \beta$ transformation was lowered to about 500°C. Later it was pointed out by Osmond, who determined the critical points of several steels used by Hadfield, that, at least in very low carbon steels, the critical points are essentially the same in tungsten steel as in carbon steels of the same hardness, but that if the temperature of heating is carried on up to higher temperatures, first Ar_1 and then Ar_2 and Ar_3 are lowered, so that Ar_2 and Ar_3 tend to join or unite with Ar_1 . Thermal analysis of a sample of Mushet's steel (carbon 1.65, silicon 1.36, manganese 2.12, tungsten 5.80, chromium 0.45) showed that the critical points of this steel were raised somewhat by increasing the maximum heating temperature and that they were diminished very greatly in magnitude, so much so that on cooling from 1300°C. in the furnace the steel showed practically no heat effect and was very hard after the treatment. A straight tungsten steel, known as "Allevard" (carbon 0.42 per cent., manganese 0.29 per cent., tungsten 6.22 per cent.), in contrast to the Mushet steel, was not hardened by heating to 1300°C. and slowly cooled. Ar_1 was markedly lowered but its magnitude was not altered. The efficacy of a high heating temperature in the heat treatment was brought out and it was shown that, by heating to a high temperature, altogether different effects were produced than by merely heating to the ordinary temperature of from 800 to 900°; but it remained for Taylor and White to make practical application of the properties of this material. It is clear from this early work that the tungsten steels behave quite differently from the carbon steels, although it seems now that this difference is more quantitative than qualitative.

This effect has also been noted by Boehler² who studied the critical points of a tungsten steel containing 0.895 per cent. carbon and 7.78 per cent. tungsten. When this steel was not heated above 1000° the pearlite transformation point occurred at about 700°C., but as soon as the heating temperature exceeded 1000°C. a second and lower critical point at 550°C. was noted. As the heating temperature was increased, the higher critical point gradually decreased in magnitude while the lower critical

¹ *Journ. Iron and Steel Inst.*, 1890, No. 1, p. 61.

² *Rev. de Met.* Abstracts, 1904, Vol. 1.

point, also said to correspond to the pearlite transformation point, increased in magnitude. When the heating temperature was carried above 1100° the lower critical point was the only one to take place on cooling. This behavior was said to be due to the tungsten and, as the tungsten increased, the temperature to which it was necessary to heat the steel to produce this effect, was increased. Increasing the tungsten also lowered the lower critical point and it was thought that a sufficient amount of tungsten would lower the point to below room temperature.¹

The effect of the high heating temperatures was reported on in detail by Swinden.² The series of steels used contained a uniform tungsten content of about 3 per cent., while the carbon varied from 0.14 to 1.34 per cent. It was found that the critical points occupied their normal positions, provided the heating were not carried too high. When the heating was carried above a certain temperature, called by him the "lowering temperature" and which was found to be dependent upon the carbon content, the Ar_1 point was found to be lowered from about 690° to about $560^{\circ}C$. The Ar_3 points were found to disappear, in case the heating was carried to above the "lowering temperature," simultaneously with the complete shifting of the pearlite point to the lower temperature. Ar_2 in the mild steels is not lowered even after heating to above $1270^{\circ}C$.; Ar_2 is raised if anything by increasing the heating temperature. Heating curves were also taken of the steels and it was noted that the Ac_1 point is higher in this series than in carbon steels. Following a high heating temperature, the critical points of the lower carbon steels were not altered appreciably but the heat effect appeared to be much greater at the lower part of the range than when the previous heating temperature was below the "lowering temperature," although the beginning of Ac_3 was found to come at about $725^{\circ}C$. in all the steels. The Ac_3 point was never very distinct but as the carbon content increased, it was undoubtedly lowered until it coincided with Ac_1 . In the steel containing 1.07 per cent. carbon the Ac point was practically independent of the previous history. The cooling curves of the steel containing 1.24 per cent. carbon and 3.02 per cent. tungsten again brought out the

¹ This was further studied and verified by CARPENTER, *Journ. Iron and Steel Inst.*, 1905, No. 1, p. 433, to whose work we shall have occasion to refer at greater length.

² *Journ. Iron and Steel Inst.*, 1907, No. 1, p. 291.

effect of the lowering temperature. When the heating was carried up to about 1100°C. there was practically no measurable displacement of the Ar_1 point. Heating to just above 1200°C. caused a lowering of Ar_1 of over 100°C. This has been explained by Osmond on the basis of the slow dissolution of the free carbide in the austenite which requires a relatively high temperature for its completion.

Swinden points out that if elementary dissolution of the carbide alone were involved, the Ar_1 point would hardly remain unaffected by heating to temperatures as much as 400° above the original Ac_1 point. He assumes, therefore, that there must be some further change in the steel at the lowering temperature involving the tungsten, but this contention is not supported by thermal evidence. He suggested later that at this temperature

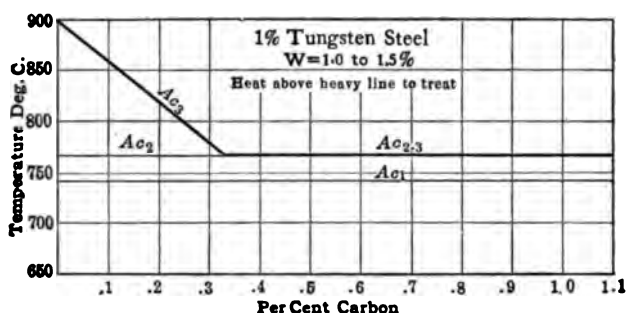


FIG. 131.—Critical points of 1 per cent. tungsten steel. (Midvale Steel Co.)

a compound of iron and tungsten, Fe_3W , dissolves in the steel and that it is the solution containing this compound which has the low Ar point, or air-hardening properties, as the case may be.¹ At the low Ar transformation, this compound and Fe_3C are supposed to be simultaneously separated. The contention that a second constituent was dissolved at the lowering temperature was supported by the fact that the electrical resistivity is increased by quenching from above the lowering temperature.

It has been advanced² that these conclusions could be accepted if it were not for the experiments of Boehler according to which there is no definite lowering temperature but a gradual lowering of the transformation point as the heating temperature is raised.

¹ *Journ. Iron and Steel Inst.*, 1909, No. 2, p. 223.

² MARS, *Die Spezialstähle*, 1912, p. 287.

Boehler's works is also substantiated by that of Brayshaw,¹ according to which the normal Ar point is lowered from 716°C. to 709°C. by heating to 960°C.

Another theory for the explanation of the lowering of the Ar₁ point is that a carbide of tungsten forms at the lowering tempera-

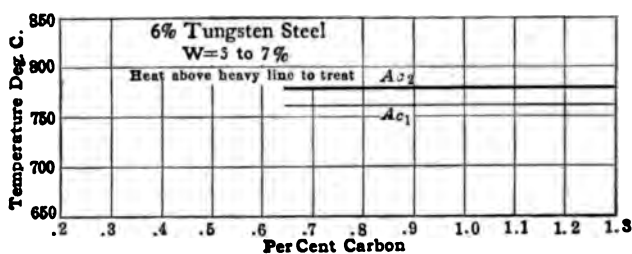


FIG. 132.—Critical points of 6 per cent. tungsten steel. (*Midvale Steel Co.*)

ture.² The weak point in these theories is that the special constituent which is supposed to form at the lowering temperature has never been identified (Carpenter).

Two critical point curves, used by the Midvale Steel Company for the heat-treatment of their 1 per cent. tungsten and 6 per cent. tungsten steels, are given in Figs. 131 and 132.

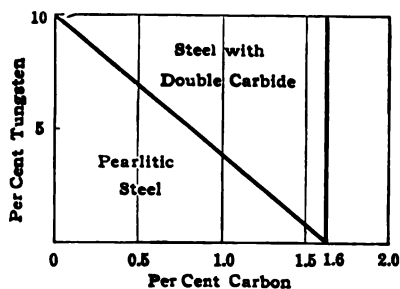


FIG. 133.—Microstructure of forged tungsten steels. (*Guillet.*)

The Microstructure of Tungsten Steels.—Guillet was the first to make a systematic study of the microstructure of the tungsten steels.³ He divided the steels into two groups as shown in Fig. 133.

¹ *Trans. Inst. Mech. Eng.*, 1910.

² *Journ. Iron and Steel Inst.*, 1908, No. 2, p. 130.

³ *Bull. Soc. d'Encourag.*, 1904, Vol. 106, p. 263; *Genie Civil*, 1904, Vol. 45, p. 7. *Journ. Iron and Steel Inst.*, 1906, No. 2, p. 10.

Two series of steels were examined containing about 0.1 per cent. carbon and 0.80 per cent. carbon. The first additions of tungsten to steel, as heretofore, produce steels whose microstructure is similar to that of ordinary steel except that the grain is much finer. This grain refinement is a special characteristic of tungsten steel. Guillet remarks that the microstructure of the tungsten steels is quite simple and strictly comparable to that of carbon steels, but that the nature of the "special constituent" or the carbide is in doubt. His researches show that the point at which the carbide first makes its appearance on addition of tungsten or carbon depends upon the sum, carbon + tungsten



×100

FIG. 134.—Microstructure of forged tungsten steel containing 0.5 per cent. carbon and 5 per cent. tungsten.

so that it would seem to be a carbide. It also has the properties of cementite — it is hard and is colored dark by sodium picrate, and is produced by carburizing a pearlitic steel.

Swinden's 3 per cent. tungsten steels also showed fairly normal structures, somewhat finer grained than the corresponding carbon steels. The Widmanstaettian structure was quite apparent in the cast steels. The eutectoid point comes at the same point as in carbon steels. The steel containing 1.07 per cent. carbon showed a definite cementite network structure both when cast and when rolled. Figure 134 is added to show the refining action of tungsten in slowly cooled steel.

From a paper which appears to be very important, but to

which the writer has not had access, the following will be summarized.¹ Annealed tungsten steel (900°C.) may contain, according to percentages of tungsten and carbon present, from two to four of the following constituents: Ferrite; double carbide, $4\text{Fe}_3\text{C}.\text{WC}$; Fe_3C ; WC ; Fe_2W ; solid solution of Fe_2W in Fe. The presence of Fe_3C and $4\text{Fe}_3\text{C}.\text{WC}$ can be determined by magnetic analysis, the critical temperature of the former being 215°C. and of the latter 400°C. If the carbon and tungsten are both low, only the Ar_1 transformation is lowered by the presence of tungsten whereas in low tungsten steels with medium carbon, both the Ar_1 and the $\text{Ar}_{2,3}$ points are lowered, in agreement with the work of Swinden.

The conclusion that tungsten merely hinders the Ar_1 transformation in taking place and, therefore, lowers it (Osmond, Boehler) is not sufficient to account for the complicated behavior of these steels, although the theories of Edwards and Swinden are also insufficient. Pure iron can dissolve as much as 9 per cent. tungsten and any excess forms Fe_2W which appears in the form of globules, sometimes mistaken for a carbide. Since part of the carbon forms WC , more tungsten is required to produce Fe_2W in proportion as the carbon content increases. In the normal condition this tungsten carbide forms the double carbide with cementite. At temperatures above Ac_1 , it dissociates into the simple carbides and if the heating is not carried very high they reassociate again on cooling and the pearlite change takes place at its normal temperature. By heating to higher temperatures, however, the tungsten carbide reacts with some of the iron present with the formation of the tungstide and a certain amount of cementite. It is the formation and dissolution of the tungstide in austenite which causes the lowering of the transformation temperature on cooling. That the lowering is due to the action of tungsten is shown by the fact that the completely lowered Ar_1 point depends on the tungsten content and not on the carbon content, although when more than 9 per cent. tungsten is present Ar_1 remains constant at about 440°C. Reheating the steel shifts the lowered Ar_1 point to just below the Ac_1 point and cooling causes the transformation to take place at the normal temperature. In this case the Ar reaction is the same as the Ac reaction, only it goes in the opposite direction. Under these

¹ HONDA and MURAKAMI, *Chem. Abstracts*, 1918, Vol. 12, Pt. 2, p. 1753. Original, *Sci. Rep. Tohoku Imp. Univ.*, 1918, Vol. 6, p. 235.

circumstances the Ar_1 point, although it comes at a high temperature, is lowered by increasing the rate of cooling. The high Ar_1 point seems to be the normal transformation point (on cooling) for tungsten steel, inasmuch as steel which is cooled very slowly from the lowering temperature to 700°C . transforms at this temperature instead of at about 400°C .

The Carbide in Tungsten Steel.—This subject has been dealt with either directly or indirectly by various investigators, and in particular by Arnold and Rhead.¹ The following points are taken largely from this paper. Up to the time of the work of Arnold and Rhead, Carnot and Goutal² had obtained a double carbide, $\text{Fe}_3\text{C}.\text{WC}$, from two steels containing 2 per cent. carbon and 6 and 7.8 per cent. tungsten respectively. They further obtained a residue whose composition corresponded to Fe_3W when a steel with 0.4 to 0.6 per cent. carbon and 6.0 per cent. tungsten was treated with hydrochloric acid. The steels used by Arnold and Rhead contained about 0.7 per cent. carbon and from 2.38 to 26.9 per cent. tungsten, other constituents being low. The bars were annealed so that the carbide could be more easily separated for analysis. The authors concluded that up to about 11 per cent. tungsten, tungsten forms a carbide WC, which is mechanically mixed with Fe_3C . This does not agree with the subsequent work of Honda and Murakami, who, it will be remembered, assume a double carbide, $4\text{Fe}_3\text{C}.\text{WC}$. At 11 per cent. tungsten, Fe_3C is expelled so that, with higher tungsten content, the carbon is present as WC and the compound Fe_2W is formed. This contention is supported neither by the microstructure nor by the chemical tests. The photomicrographs are labeled as containing crystals of WC which have etched dark with sodium picrate, but positive identification is lacking.

Ruff and Wunsch, experimenting with pure carbon-tungsten alloys, secured evidence which indicated that W_3C , W_2C and WC form at high temperatures. The equilibria were found to be very complicated; for example, a pseudo-ternary eutectic was noted, as well as a peculiar decomposition of the carbide WC into graphite and W_3C and a small amount of W_2C , when heated to below its melting point.³

¹ *Proceed. Inst. Mechanical Engineers*, March 20, 1914.

² *Compt. Rend.*, 1899, Vol. 128, p. 208.

³ *Zeit. anorg. Chemie*, 1914, Vol. 85, p. 292.

The Heat Treatment and Mechanical Properties of Tungsten Steel.—The results of Hadfield's tests are given in Table 106.

TABLE 106.—MECHANICAL PROPERTIES OF TUNGSTEN STEEL

No.	Composition		Condition	Yield point, lbs. per sq. in.	Tensile strength, lbs. per sq. in.	Elongation, per cent.	R. A., per cent.
	C	W					
A	0.12	0.10	Not annealed.....	44,700	55,500	35	60
			Annealed.....	31,400	49,300	43	65
B	0.15	0.20	Not annealed.....	49,300	60,400	40	60
			Annealed.....	35,800	49,200	46	66
C	0.15	0.40	Not annealed.....	53,700	69,400	33	59
			Annealed.....	40,300	56,000	39	60
D	0.13	0.35	Not annealed.....	44,800	60,400	37	58
			Annealed.....	35,800	51,500	45	69
E	0.21	0.81	Not annealed.....	65,000	71,600	35	63
			Annealed.....	40,300	58,315	37	53
F	0.22	1.20	Not annealed.....	56,000	71,600	25	49
			Annealed.....	38,000	60,400	37	54
G	0.21	1.49	Not annealed.....	44,700	76,200	26	46
			Annealed.....	42,000	62,700	37	54
H	0.28	3.40	Not annealed.....	69,400	91,800	29	51
			Annealed.....	51,480	76,100	34	53
I	0.38	7.47	Not annealed.....	82,900	141,000	14	18
			Annealed.....	53,700	89,606	25	38
J	0.46	8.33	Not annealed.....	100,000	143,300	2	2
			Annealed.....	56,000	94,000	23	32
K	0.63	10.56	Not annealed.....	123,000	179,212	5	4
			Annealed.....	62,700	107,500	10	10
L	0.76	15.65	Not annealed.....	Could not	be forged.		
			Annealed.....	60,400	127,600	3	2
M	0.78	16.18	Not annealed.....	112,000	123,100	0.5	0.25
			Annealed.....	60,400	96,000	1	0.75

The elastic limit, especially of the annealed specimens, was found to be surprisingly low for a steel containing tungsten, an element which is known to confer such great hardness on steel. Tungsten, therefore, operates differently from nickel, chromium and manganese. The properties of the heat treated, that is quenched and tempered, tungsten steels were not determined.

In the discussion Harbord and Guillet reported the results of their work on tungsten steels. Guillet,¹ in connection with his work on the special steels, found that tungsten increases both the tensile strength and elastic limit of the pearlitic steels and lowers the ductility.

The heat treatment of the tungsten steels is quite similar to that of the carbon steels although the effect of quenching is

¹ *Genie Civil*, 1904, Vol. 45, p. 7; *Alliages Metalliques*, p. 332.

somewhat more intensive. According to Guillet, increasing the quenching temperature of the carbide steels tends to cause the disappearance of the double carbide. The mechanical properties of the pearlitic steels are affected by heat treatment in the same manner as carbon steels of the same carbon content. The carbide steels are differentiated from the corresponding pearlitic steels by their lower tensile strength. The resistance to shock of forged steels was found to diminish as the tungsten increased. The influence of tungsten in heat treated steels was found to be considerable; also that it increases with increase in the tungsten content. Guillet noted no dissociation of the double carbide of iron and tungsten (which he assumed) by heating to 850°C. but he found that carbide steel was made much milder by this treatment. Quenching from above 850°C. caused the dissolution of the "double carbide." These steels showed a fine-grained martensitic structure which was very strong and extremely hard.

Guillet gives very little regarding the mechanical properties of heat treated tungsten steel. One steel containing carbon 0.47, manganese 0.22 and tungsten 0.60 had the following properties in the normal state—tensile strength 111,479 lbs. per sq. in.; elastic limit 85,339 lbs. per sq. in.; elongation 14 per cent. When quenched and tempered at 500°C., the steel had the following properties—tensile strength 142,232 lbs. per sq. in.; elastic limit 119,125 lbs. per sq. in.; elongation 7 per cent. He did not believe that this steel possessed any great advantage over other steels and its high price would make it all the less desirable; furthermore, its resistance to shock in the heat treated state was not exceptionally high.

Swinden carried out a fairly complete series of tests on steels which had been normalized by heating to 950°C. and cooled in air. The results of his tensile tests are given in Table 107.

The results of the alternating stress tests show that tungsten is not a very desirable element from this point of view. It was remarked that an average standard boiler plate test is about 350 alternations.

These tests as well as those of other experimenters, show that tungsten acts on steel in an indirect way, *i.e.* its principal effect is on the condition of the carbon and the grain of the steel, but not on the iron proper. Arnold and Rhead in their paper also report on the mechanical properties of the tungsten steels used

for their carbide determinations but inasmuch as their steels were drastically annealed, the results will not be contributed here.

TABLE 107.—MECHANICAL PROPERTIES OF THREE PER CENT. TUNGSTEN STEEL

Analysis		E. L., lbs. per sq. in.	Max. stress, lbs. per sq. in.	Elong., per cent. on 2 in.	R. A., per cent.	Alt. stress test	Remarks on fracture
C	W						
0.144	3.25	54,656	76,608	28.5	62.5	218	Dull grey granular, cup and cone with deep silky edges.
0.218	3.24	56,500	74,000	27.5	61.0	226	Very similar to first.
0.27	2.92	64,960	88,000	24.1	59.8	232	Similar to foregoing.
0.48	3.11	93,000	120,300	16.0	45.5	96-94	Still granular with silky edges.
0.53	3.18	100,800	124,990	16.0	47.9	104	Rather lighter, but still granular.
0.57	3.17	77,400	129,200	14.5	44.2	92	As one preceding.
0.80	3.08	109,312	138,880	13.5	29.5	42	Extremely finely crystalline. Flatter, but still traces of silky edges.
1.07	3.09	90,300	113,792	15.5	28.2	30	Very finely crystalline. Flat.
1.24	3.02	103,100	125,440	9.5	16.9	24-20	Very finely crystalline.

Hardness of Tungsten Steel.—It is true that tungsten steel is of commercial importance primarily because of its great cutting hardness, in combination with considerable toughness, when in the properly heat treated condition, but in technical practice the hardness of the annealed steels is also of considerable moment. According to Guillet, tungsten increases the hardness of steel in the forged state up to about the point at which the double carbide enters, above which point the hardness is more or less irregular. This increase in hardness is naturally reflected in an increase in the difficulties of forging and machining tungsten steel. This effect is brought out in the results of Hadfield on forged and annealed tungsten steels.

Mars, in connection with his work on the magnetic properties of tungsten steel, measured the hardness and his results are given in Table 108. These steels are very hard but their great virtue lies in the degree to which they combine cutting hardness with toughness, and with which they retain this hardness when cutting at high speeds.

Tungsten, as compared to chromium, has a much smaller effect in increasing the depth of penetration of hardness, and

bars of tungsten steel, after hardening, are apt to show a soft core. This effect is shown at once by the appearance of the fractured surface. However it does not seem as if all of the possibilities of tungsten steel have been worked out in technical heat treatment, particularly the utilization of the principle of the lowering temperature.

The Magnetic Properties.—It was early recognized that tungsten steel has an exceptionally high retentivity.¹ Hadfield pointed out that it is necessary to have a considerable amount of carbon present in tungsten steel in order to confer permanent magnetism. This is because tungsten *per se* has an inappreciable effect, and confers magnetism only through carbon.

In mild steels tungsten has a very small effect either on the permeability or on the electrical conductivity of iron, less than that of any of the other elements commonly added to iron. The addition of tungsten also causes only a slight decrease in the induction, but in high carbon steels it produces a great increase in hysteresis, by increasing both the remanent magnetism and the coercive force. These facts combine to make tungsten steel especially suitable for use as permanent magnets when properly heat treated.²

Mme. Sklodowska-Curie³ examined the magnetic properties and heat treatment of tungsten steels and was among the first to point out their importance in the construction of permanent magnets. Mme. Curie found a coercive force of 60 or above for ordinary steel and values of 70 to 74 for tungsten steel and of 80 to 85 for molybdenum steel, which behavior, at that time, was held to be most remarkable.

The improvement in the properties of magnet steel produced by the addition of tungsten hold only up to a certain percentage of tungsten, above which point the magnetism again falls off. As compared to other ternary steels which might be used for permanent magnets, the tungsten steels possess the advantage of lower cost, on the one hand, and of better properties, on the other.⁴ The improvement in magnetic properties up to about

¹ See for example, HEPPE's article cited.

² BARRETT, BROWN and HADFIELD, *Scientific Trans. Royal Soc., Dublin*, 1900.

³ *Electrician*, 1898, Vol. 15, p. 28.

⁴ HANNACK, *Stahl u. Eisen*, 1908, Vol. 28, p. 1237.

5 per cent. tungsten has been confirmed by Mars, whose results are summarized in Table 108.¹

TABLE 108.—MAGNETISM AND HARDNESS OF TUNGSTEN STEEL

Analysis		Hardening temp., °C.	Quenched	Brinell hardness	Magnetism		
C	W				Units on magnetometer scale		
					Immediately after magnetising	After 8 days	Loss in magnetism, per cent.
1.15	0.68	680	H ₂ O at 10-15°C....	600	69.5	68.8	2.9
1.16	1.20	750	H ₂ O at 10-15°C....	744	76.5	76.0	1.3
0.64	1.12	820	H ₂ O at 10-15°C....	713	76.5	73.5	3.9
0.62	1.96	800	H ₂ O at 10-15°C....	782	85.5	84.0	1.8
1.20	3.22	740	H ₂ O at 10-15°C....	782	66.5	65.0	4.5
0.57	5.47	930	H ₂ O at 10-15°C....	782	90.5	90.5	0.0
1.25	8.65	930	H ₂ O at 10-15°C....	782	61.0	58.5	4.1
ca	ca						
1.25	30.0	850	Oil.....	578	19.0		

Mars found an increase in magnetism for the tungsten steels over that of carbon steels of from 20 to 50 per cent., with a maximum retentivity at about 0.6 per cent. carbon and 5 per cent. tungsten, which agreed with the composition universally employed for permanent magnets (Mn = 0.26). This steel when quenched from 900°C. in water showed a Brinell hardness of 782 and a magnetism corresponding to 90.25 units on the magnetometer as compared to a Brinell hardness of 600 and 58.5 units for a carbon steel containing 0.65 per cent. carbon and 0.12 per cent. manganese quenched from 850°C., agreeing with the figures of Mme. Curie obtained with an Allevard steel. Its specific gravity is 8.13 in the forged state and 8.08 in the normal hardened state. It is brittle and has a tensile strength of 192,000 lbs. per sq. in. A hardening temperature of 950°C. (held 10 minutes, quenched in water at 15°C.) was found to produce the highest remanent magnetism which was equal to 94 units on the magnetometer; after 48 hours it was found to be 92.5 units or lower by 1.6 per cent. Higher hardening temperatures made the steel coarser grained thereby lowering the remanent magnetism. The extremely fine grain undoubtedly improves the magnetic properties inasmuch as this magnet steel when hard-

¹ *Stahl u. Eisen*, 1909, Vol. 29, p. 1673 and p. 1769.

ened at 930°C. is very fine grained and resembles troostite. The steel when quenched from 1200°C. has a coarse martensitic structure.

Mars explains the exceptional qualities of tungsten steel as due to the presence of a comparatively large amount of free iron in the tungsten steel, combined with the glass hardness. The free iron is necessary to secure the requisite amount of induced magnetism while the hardness (here synonymous with cohesion or viscosity) is necessary in order that the maximum amount of induced magnetism may be retained as remanent magnetism when the magnetizing force is removed.¹

The magnetic transformations of a number of tungsten steels such as would be used for permanent magnets have been determined by Mme. Curie. They are given in Table 109.

TABLE 109.—THE MAGNETIC TRANSFORMATION POINTS OF TUNGSTEN STEEL

Composition		Transformation points	
C	W	On heating	On cooling
0.76	2.7	746	714
1.02	2.7	721	684
1.11	2.7	725	687
0.55	2.9	750	708
1.53	3.5	722	696
0.59	5.5	740	705
1.96	7.7	732	697

¹ Among other work on the magnetic properties of tungsten steel may be mentioned the following. ABT (*Annalen de Phys.*, 1901, Vol. 6-4, p. 774), reported on the magnetic properties of certain ternary steels which had been on exhibition at the Paris Exposition in 1900. He noted in particular that the magnetism had decreased very appreciably while away from the laboratory. It was pointed out by BROWN, in a research on steels for permanent magnets, that the loss of magnetism found by ABT was very high and due probably to too high tungsten content (*Proc. Royal Scient. Soc.*, Dublin, 1910, Vol. 12, p. 312). On the other hand, tungsten steel properly selected and heat treated varies in magnetism but little with time and soon becomes permanent, a point which is verified by the work of MARS. SWINDEN (*Journ. Inst. Elec. Eng.*, 1909, Vol. 42, p. 641) found that 3 per cent. tungsten has a small effect on the magnetic properties of low-carbon steel and that the remanent magnetism increases with carbon up to a maximum at 0.5 to 0.6 per cent. carbon. The steel with 0.5 per cent. carbon is very greatly improved by hardening.

The specific gravity of tungsten steel increases perceptibly with the tungsten content as is given in the following table taken from Hadfield's work.

TABLE 110.—SPECIFIC GRAVITY OF TUNGSTEN STEEL

Per cent. carbon	Per cent. tungsten	Specific gravity
0.15	0.20	7.676
0.21	1.49	7.683
0.28	3.40	7.792
0.46	8.33	8.109
0.78	16.18	8.602

The Uses of Tungsten Steel.—The simple tungsten steels are used principally on account of their exceptional hardness, both mechanical and magnetic. High grade chisel steel contains from 1 to 2 per cent. tungsten and from 0.30 to 1.0 per cent. carbon depending upon the specific properties required. Tungsten steel is also very valuable as a finishing steel for such work as the finishing of rifle barrels, etc. For this purpose, steel containing from 3 to 6 per cent. tungsten and about 1.2 per cent. carbon is used. This steel takes and retains a keen cutting edge and is greatly superior to carbon tool steel. Steel used in the manufacture of liners for Howitzers and other guns contains from 1 to 3 per cent. tungsten and 0.6 to 0.7 per cent. carbon. Tungsten steel is quite commonly used for poppet valves in gasoline engines. This steel contains about 0.50 to 0.60 per cent. carbon, 1.50 to 2.00 per cent. tungsten and a small amount of chromium.

MOLYBDENUM STEEL

Molybdenum, as a metal, is very similar to tungsten and, as one would expect from their positions in the periodic system, these two metals have very much the same effect on steel. Quantitatively, it has been found that one part of molybdenum, by weight, confers about the same properties on steel as two to three parts of tungsten. The molybdenum steels, however, have not been used very extensively, due partly to the relatively high price and scarcity of molybdenum and partly to the metallurgical difficulties involved in the production of the steels free

from brittleness and scaininess. Considerable of the difficulty encountered has been due to the molybdenum used which is very apt to contain injurious impurities. Chromium and tungsten steels are almost universally used for those purposes for which molybdenum steel, on account of its properties, would find an application. That it is not impossible to produce molybdenum steel satisfactorily is evidenced by the fair amount of this steel which has been made in the past and particularly during the recent war. The greatest success from the use of molybdenum appears to have been secured from its addition to other special steels.

The Constitution of Molybdenum Steel.—The iron-molybdenum alloys have many points in common with the iron-tungsten alloys.¹ For our purposes we can safely assume that small amounts of molybdenum lower the melting point of iron and that the alloys so made are homogeneous solid solutions. Above about 30 per cent. Mo the constitution is complicated by the existence of $\text{Fe}_3\text{Mo}_2(?)$,² the formation of which depends upon the molecular condition of the melt. If the compound does not form properly, a metastable and pseudo-ternary system forms which introduces a hard constituent, in increasing amount as the percentage of molybdenum increases.

From what little work has been done on the critical points of molybdenum steel, it seems clear that molybdenum has about the same effect as tungsten.

Mme. Curie³ determined the (magnetic) transformation points of three steels containing 0.51, 1.25, and 1.72 per cent. carbon and 3.5, 3.4, and 3.9 per cent. molybdenum respectively. The transformation point on heating for the first two steels was 730°C. and for the third was 720°C. while the points on cooling were 686°, 689°, and 683°C. respectively.

According to Lautsch and Tammann, there were no transformation points in their steel ($\text{C} = 0.07$ per cent.) when 1 per cent. molybdenum was added.

Carpenter has also extended his work to molybdenum steels and his results may be briefly stated by the following table.⁴

¹ LAUTSCH and TAMMANN, *Zeit. anorg. Chem.*, Vol. 35, p. 386.

² See CARNOT and GOUTAL, *Compt. Rend.*, Vol. 125, p. 221.

³ *Bull. Societe d'Encourage.*, 1898, p. 47.

⁴ *Journ. Iron and Steel Inst.*, 1905, No. 1, p. 447.

TABLE 111.—CRITICAL POINTS OF MOLYBDENUM STEEL

Composition		Heating temperature, °C.	Critical points on cooling
C	Mo		
0.28	0.95	1020	812°; 759°; 688°
		1250	836°; 617°; 546°
0.57	9.25	900	768°; 688°
		1200	783°-706°; 592°-385°

The first systematic examination of the microstructure of molybdenum steel was that of Guillet.¹ He found results similar to those for tungsten steels but that, as compared to tungsten, only about one-fourth the amount of molybdenum was required to produce a similar effect. The results are given in Fig. 135.

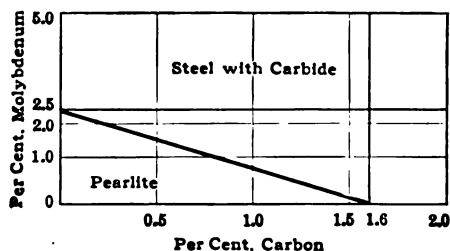


FIG. 135.—Microstructure of forged molybdenum steel. (Guillet.)

Swinden reported that molybdenum makes pearlite very fine grained so that in most cases the structure is not resolved at a magnification of one hundred-fifty diameters. The eutectoid point, called the "saturation point" in the paper, is lowered by the addition of molybdenum until at 8 per cent. molybdenum it comes at about 0.4 per cent. carbon. No special constituent was detected but cementite in a peculiar worm-like structure was noted in the annealed steel.

The work on the carbide constituent found in molybdenum steel, as reported in the literature, is somewhat contradictory. In steels containing about 2 per cent. carbon and 4 per cent. molybdenum, Carnot and Goutal found a double carbide corresponding to the formula $\text{Fe}_3\text{C}.\text{Mo}_2\text{C}$. A molybdenum carbide,

¹ *Compt. Rend.*, 1906, Vol. 142, p. 889 and 928; also *Genie Civil*, 1904, Vol. 45, p. 242.

Mo_2C has also been found by Niclardot¹ and the double carbide has been verified by Williams.

Arnold and Rhead, continuing their work on the carbides,² have investigated the composition of the carbide constituent found in molybdenum steel. They state that when 18.25 per cent. molybdenum is present, Fe_3C disappears and $\text{Fe}_3\text{Mo}_2\text{C}_2$, a double carbide and very stable, takes its place. Molybdenum does not appear to form a compound with iron corresponding to Fe_2W . They state that the steel hardening power of molybdenum is several times that of tungsten but that it is not as reliable to the metallurgist.

Guillet in his early work noted a structure resembling a eutectic in the alloys containing 10 per cent. molybdenum. This he said might be ferrite and the double carbide. He concluded that the special constituent was a double carbide the same as in tungsten steel.

Swinden in his work on carbon-molybdenum steels,³ isolated and analyzed the carbide, although no definite conclusion can be drawn from his work. It was shown that the molybdenum in the carbide increases as the molybdenum in the steel increases, but that, with constant molybdenum, as the carbon increases, the percentage of molybdenum in the carbide decreases. The author concluded that the carbon probably exists as Fe_3C , and the molybdenum as a compound of iron which may be partially decomposed by electrolysis.

The Heat Treatment and Mechanical Properties of Molybdenum Steel.—According to both Hadfield⁴ and Guillet⁵ molybdenum produces a marked increase in both the elastic limit and tensile strength but leaves the steel both ductile and tough, the latter property as shown by impact tests. Heat treatment has the same effect on the properties as it has on carbon steel. The double carbide steels are strong but are too brittle to be of any value except on account of their hardness. Guillet's statement that only the pearlitic steels are capable of being rolled and forged, in the light of Swinden's work, needs to be modified.

The properties of tungsten steel and molybdenum steel were

¹ *Metaux Secondaries*, 1908, p. 90.

² *Engineering*, 1915, Vol. 100, p. 555.

³ *Iron and Steel Inst., Carnegie Sch. Mem.*, 1911, Vol. 3, p. 66.

⁴ *Journ. Iron and Steel Inst.*, 1904, No. 1, p. 30.

⁵ *Alliages Metalliques*, 1906, p. 340; *Loc. cit.*

TABLE 112.—MECHANICAL PROPERTIES OF MOLYBDENUM STEEL

Composition		Condition	Elastic limit, lbs. per sq. in.	Tensile strength, lbs. per sq. in.	Elongation, per cent. on 2 in.	R. A., per cent.	B. H. No.	Scl. No.	Arnold's No.
C	Mo								
0.19	1.03	As rolled.....	50,176	75,040	33.31	64.32			
		Annealed.....	31,136	58,500	35.50	65.75	99	11	336
		Hardened and tempered.....	49,056	90,048	27.46	68.40	241	a33 b27	301
0.44	1.05	As rolled.....	77,056	121,632	19.5	49.23			
		Annealed.....	40,992	79,968	25.0	39.2	131	13	210
		Hardened and tempered.....	168,449	210,560	14.08	49.2	387	a45 b37	137
0.87	1.02	As rolled.....	116,480	179,200	14.5	34.36			
		Annealed.....	58,240	120,960	17.22	22.25	228	23	103
		Hardened and tempered.....	193,536	240,300	9.15	25.2	418	a61 b44	92
1.21	1.09	As rolled.....		131,264	1.0	2.02			
		Annealed.....	58,240	95,424	5.55	7.5	207	22	14
		Hardened and tempered.....	203,840	278,880	4.92	12.0	512	a61 b45	71
0.25	2.18	As rolled.....		117,824	21.05	57.0			
		Annealed.....	31,584	64,960	33.3	62.5	116	15	370
		Hardened and tempered.....	115,360	171,136	15.49	54.4	387	a36 b35	172
0.44	2.18	As rolled.....		150,976	16.7	46.41			
		Annealed.....	43,232	82,208	27.7	44.3	143	18	259
		Hardened and tempered.....	148,960	211,456	14.08	47.2	444	a47 b39	103
0.88	2.19	As rolled.....	129,024	198,912	12.1	32.07			
		Annealed.....	54,656	107,072	18.8	27.5	207	22	126
		Hardened and tempered.....	178,752	260,736	5.63	12.0	512	a62 b47	80
1.21	2.11	As rolled.....	169,344	216,832	7.04	9.6			
		Annealed.....	61,600	95,200	9.4	13.5	196	22	27
		Hardened and tempered.....		270,816	512	a69 b48	39
0.19	4.11	As rolled.....	75,264	119,168	21.70	52.71			
		Annealed.....	33,360	64,960	42.7	72.5	116	17	366
		Hardened and tempered.....	66,304	88,032	30.2	64.0	286	a31 b28	329
0.49	4.01	As rolled.....	120,064	188,160	13.5	33.81			
		Annealed.....	42,112	77,056	28.3	52.0	143	18	247
		Hardened and tempered.....	139,776	188,832	11.26	41.6	444	a52 b43	109

Composition		Condition	Elastic limit, lbs. per sq. in.	Tensile strength, lbs. per sq. in.	Elongation, per cent. on 2 in.	R. A., per cent.	B. H. No.	Sel. No.	Arnold's No.
C	Mo								
0.86	4.00	As rolled.....		230,272	8.0	17.27			
		Annealed.....	45,920	94,304	20.5	34.0	179	20	146
		Hardened and tempered.....	203,840	258,048	4.22	4.8	512	a62 b44	52
1.06	4.02	As rolled.....	179,872	239,232	10.56	18.40			
		Annealed.....	42,560	92,060	15.5	20.5	196	23	66
		Hardened and tempered.....	267,008	282,240	7.04	23.2	532	a68 b48	45
0.13	8.01	As rolled.....		92,288	25.7	52.22			
		Annealed.....	41,664	79,072	31.1	58.75	143	16	283
		Hardened and tempered.....	53,760	81,984	30.9	65.60	163	a16 b15	239
0.36	8.17	As rolled.....		148,288	19.4	45.89			
		Annealed.....	34,720	77,056	36.6	68.23	143	18	273
		Hardened and tempered.....	75,264	105,280	25.3	54.40	351	a33 b30	226
0.44	8.11	As rolled.....	154,112	215,040	19.71	34.0			
		Annealed.....	38,528	83,104	32.22	57.5	156	18	215
		Hardened and tempered.....	77,728	127,232	21.1	49.2	444	a40 b39	122
0.77	7.85	As rolled.....	148,960	193,700	9.85	18.4			
		Annealed.....	45,023	87,584	22.2	35.5	170	20	108
		Hardened and tempered.....	216,832	256,296	7.74	23.2	512	a55 b42	33
1.12	7.92	As rolled.....	189,952	245,504	8.45	16.40			
		Annealed.....	48,832	92,288	16.1	24.00	187	22	66
		Hardened and tempered.....					512	a68 b46	24
1.36	2.54	As rolled.....	172,032	184,128	2.11	2.4			
		Annealed.....	47,040	89,600	7.22	7.5	196	26	16
		Hardened and tempered.....		179,200	nil	nil	532	a61 b44	10

For scleroscope hardness, a = hardened, b = tempered. Quenching temperatures varied as follows: C, 0.2-950°C.; C, 0.5-900°C. C, 0.8-850°C. C, 2-800°C.; all $\pm 10^\circ\text{C}$. Bars were held 15 min. at temperature and quenched in oil at 35°C. The bars were tempered at 550°C. $\pm 10^\circ\text{C}$. for 15 min. in lead and cooled in air. Annealing was carried out in closed tubes and consisted in holding at 950°C. for two hours and cooling to 900°C. in 5 hours and from 900°C. to 60°C. in about 62 hours.

Elongations are comparable with tests on bars 2 in. long and 0.654 in. in diameter.

early compared by Lipin,¹ but the results of his tests will not be reproduced here as there is considerable doubt as to the purity of his materials and therefore as to the quality of the steels used.

¹ *Stahl u. Eisen*, 1897, Vol. 17, p. 571.

He pointed out that the most valuable property of molybdenum steel seems to be its power of hardening without cracking.

Swinden determined the mechanical properties of four series of steels containing 1, 2, 4, and 8 per cent. molybdenum and about 0.2, 0.45, 0.85 and 1.15 per cent. carbon for each molybdenum percentage. He found the steels to be very susceptible to heat treatment and that slow cooling from 950°C. practically ruined them. Molybdenum has a strong influence on quenched and tempered steels. The steels which possess the most suitable mechanical properties were the 1 and 2 per cent. steels. The results of his tests are summarized in Table 112.

In this paper the theory is advanced that the molybdenum is dispersed in the ferrite as a solid colloidal solution of an iron-molybdenum compound in iron. Heating to 1200°C. causes the iron-molybdenum compound to pass into solid solution and at the same time the transformation on cooling is lowered as it is in tungsten steel. The properties of commercial molybdenum steel containing chromium will be given later.

The Magnetic Properties.—Molybdenum steel resembles tungsten steel in magnetic properties and makes very excellent permanent magnets. On account of the reasons mentioned above, however, tungsten steel is generally used in preference to molybdenum steel for this purpose.

The Electrical Conductivity.—It was early determined by Le Chatelier that the addition of molybdenum to iron has a very small effect on the electrical conductivity. This would indicate that molybdenum is not in solid solution in iron. Both Swinden¹ and Boudouard² have verified the work of Le Chatelier³ who also found that as in the case of tungsten steel, the resistivity appears to be practically independent of the condition of the steel, whether forged, annealed, or heat treated (in the usual manner). Swinden found the resistivity of his steels to run about as follows: carbon ca. 0.2 per cent.—14 to 19; carbon ca. 0.45 per cent.—15 to 20; carbon ca. 0.85 per cent.—16 to 21; and carbon ca. 1.2 per cent.—17 to 22 in microhms per centimeter cube. Quenching molybdenum steels from 1200°C. altered the material in that it materially increased the resistivity. This increase in resistivity is greater as the molybdenum content increases. Swinden took this as

¹ *Loc. cit.*

² *Compt. Rend.*, Vol. 100, No. 3, p. 1475.

³ *Contribution a l'Étude d. Alliages*, p. 418.

indicating that at least a portion of the molybdenum passed into solid solution at 1200°C.

Dupuy and Portevin, working on the thermoelectric properties of special steels,¹ noted a difference in the behavior of low carbon and high carbon molybdenum steels. They state that "in the series of steels with low carbon percentages, the influence of molybdenum on the thermoelectric force is but little appreciable so long as the percentage of molybdenum does not exceed 5 per cent. With regard to carburized steels the same form of curve is met with as for the chromium steels, so far as the variation in thermoelectric force with variation in the percentage of molybdenum is concerned. The thermoelectric force is lowered on quenching, particularly as regards the steels containing 0.8 per cent. carbon."

Uses of Molybdenum Steel.—Molybdenum steel is used in general for the same purposes for which tungsten steel is used. At times a certain amount of molybdenum is used to replace tungsten or is added to other special steels where hardness and resistance to penetration are desired. At the present writing the future of molybdenum in steel metallurgy seems to be in its use in chrome-molybdenum or chrome-nickel-molybdenum steels for automobile or air plane service where particularly high grade steels are required, and possibly in its use in high speed steel.

VANADIUM STEEL

Vanadium occupies a position in the periodic system relative to iron on the opposite side of chromium, and towards those elements which have a great affinity for both carbon and oxygen. This behavior of vanadium characterizes its influence in steel as a deoxidizing agent, although it is seldom added for this purpose, and as a hardening agent. As a hardening agent, the action of vanadium is so intensive that additions of vanadium are limited to very small amounts.

An account of the first systematic and successful experiments with vanadium in steel is of sufficient historical and general interest, it is believed, to be repeated here.² In 1900, in the first report on the effect of vanadium in straight carbon steel, the remarkable effect in increasing both the strength and the

¹ *Journ. Iron and Steel Inst.*, 1915, No. 1, p. 306.

² ARNOLD, *Journ. Iron and Steel Inst.*, 1915, No. 1, p. 442.

cutting hardness was noted. Its action was said to resemble that of tungsten but that it was many times as powerful. In subsequent reports the results of further tests were cited showing the truly remarkable behavior of this element. A theory was developed to explain the effect of vanadium, the principal points of which were that vanadium reduces the segregation of the carbide and that it probably forms a double carbide of iron and vanadium which is excessively hard. These two features may be said to characterize vanadium steel. It was also noted that vanadium added to tungsten steel or chromium steel produced a remarkable increase in the strength. Since that time there has been considerable work done on the addition of vanadium to steels, but we shall see that vanadium is generally added to some ternary or quaternary steel, such as chromium steel or high speed steel. In fact the steel usually referred to as "vanadium steel" is really a quaternary steel containing chromium and will be considered at another place.

The Constitution of Vanadium Steel.—According to Vogel and Tammann,¹ vanadium and iron form a continuous series of solid solutions. The diagram is of the Type Ib with a minimum at about 33 per cent. vanadium and 1435°C. The effect of vanadium on the transformation points of iron was not determined, but in the 10 per cent. alloy no critical points were noticed. Pütz,² who determined the critical points of vanadium steels containing up to 1 per cent. vanadium, found that the transformation point was raised 10°C. by 0.2 per cent. vanadium. Portevin³ determined the critical points of Guillet's steels containing 0.2 per cent. carbon and 0.8 per cent. carbon and from 0.2 per cent. to 7 per cent. vanadium. He found that the beginning of the ferrite segregation was raised somewhat by vanadium but that Ar_1 was lowered. Steel containing 0.8 per cent. carbon and 7 per cent. vanadium showed the recalescence point at 700°C. Portevin ascribes the effect of 0.2 per cent. vanadium found by Pütz to be due to surface decarburization of the test specimen.

McWilliams and Barnes determined the critical points of a graded series of steels with the carbon varying from 0.09 to 1.32 per cent. and a constant vanadium content of approximately 0.2 per cent. This amount of vanadium corresponds to the

¹ *Zeit. anorg. Chemie*, 1908, Vol. 55, p. 73.

² *Metallurgie*, 1906, Vol. 3, p. 649.

³ *Rev. de Met.*, 1909, Vol. 6, p. 1352.

amount which is ordinarily used in commercial practice. The work of these experimenters shows that 0.2 per cent. vanadium raises the critical points of steel and introduces considerable hysteresis ($Ac_1-Ar_1 = 60$ to $70^\circ C.$) which is extended even to the A_2 transformation point. In the medium carbon steels where A_2 and A_3 come together, the hysteresis is great enough to cause all three points to come together on heating so that on heating there is but one critical point, while on cooling there are two. The critical points as given on the heating and cooling curves are as follows:

TABLE 113.—CRITICAL POINTS OF VANADIUM STEEL. McWILLIAMS AND BARNES

Mark	C	V	Mn	Ac_1	Ac_2	Ac_3	Ar_3	Ar_2	Ar_1	Max. temp.
1241	0.09	0.16	0.21	761	815	885	871	786	686	1028
1240	0.23	0.16	0.16	757	?(a)	?(a)	812	770	700	962
1238	0.40	0.23	0.30	754	?(a)	?(a)	754	754	698	989
1235	0.56	0.21	0.30	752	?(a)	?(a)	736	736	701	1029
1263	0.71	0.22	0.31	746	?(a)	?(a)	698	698	698	1006
1260	0.98	0.21	0.38	756	756	756	698	698	698	967
1234	1.32	0.20	0.33	747	747	747	709	709	709	1062

These critical points are those recorded on the authors' curves. They correspond to the maxima and not the beginning of the heat effects. (a) This point said to be Ac_{123} . Critical points are in degrees Cent.

The microstructure of vanadium steels was first systematically investigated by Guillet. The effect of vanadium on the structure

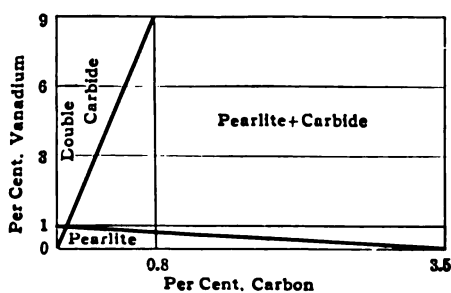


FIG. 136.—Microstructure of vanadium steel. (Guillet.)

of steel is given in Fig. 136, for steels in the forged state. Of particular interest is the very small pearlitic field, which agrees well with what is known of the mechanical properties of these steels.

Guillet noticed that vanadium steel etches differently from carbon steels in that the ferrite is colored brown on etching with picric acid. This effect increases with the amount of vanadium. In the low carbon steels ($C = 0.2$ per cent.) when more than 0.7 per cent. vanadium is added, a new constituent appears in relief on the microsection. This constituent increases as the vanadium increases up to 3 per cent. whereupon the pearlite disappears entirely. The same takes place on adding vanadium to 0.8 per cent. carbon steels. Between 0.5 per cent. and 7 per cent. vanadium the special constituent and pearlite are seen together but above 7 per cent. there is nothing but the special constituent in a uniform ground mass.

Guillet believes the special constituent to be a carbide, which is shown by cementation experiments, and by its variation in amount with the carbon content. McWilliams and Barnes remarked regarding their series of steels containing 0.2 per cent. vanadium that the structure is of a much finer texture than that of the corresponding carbon steels. It was noted in this series that the ferrite segregates into bands in the milder steels. This segregation may be eliminated by subsequent heat treatment. The eutectoid point for 0.2 per cent. vanadium lies some place between 0.71 and 0.98 per cent. carbon.

Guillet in his paper on the use of vanadium in metallurgy,¹ publishes a series of photomicrographs showing the structure of vanadium steel. These photographs show that it resembles the structure of carbon steel except when a sufficient amount of vanadium is present to produce the special constituent.

The microstructure of vanadium steel and the action of vanadium in steel necessarily involve the question of the composition of the special constituent which forms when vanadium is added. This constituent is not found unless carbon is present and it increases in amount as the carbon increases, hence presumably it is a carbide, as Guillet assumed. As for the chemical investigation of the carbides of iron and vanadium, Moissan has shown that vanadium and carbon form a series of carbides whose compositions depend somewhat upon the temperature at which they are formed. Nicolardot² isolated the carbides from vanadium steels and ferrovanadium, and obtained in low vanadium steel a product which he took to be a double carbide of Fe_2C

¹ *Journ. Iron and Steel Inst.*, 1905, No. 2, p. 118.

² *LE VANADIUM*, 1905.

and V_3C_2 or V_4C_3 . The amount of carbon in the carbide increased as the vanadium increased and as the temperature of preparation was raised. In ferrovanadium the product was carbide of vanadium— V_4C_3 or V_3C_2 .

Arnold and Read, in the course of their investigations, have likewise determined the chemical and mechanical relations of iron, vanadium and carbon.¹ They concluded, from their chemical and microscopical examinations, that iron and vanadium form no double carbide but that on adding vanadium to steel, V_4C_3 forms as a distinct phase which increases in amount (Fe_3C decreasing) as the vanadium increases. From the photomicrographs it was clear that the pearlite did not form as in annealed carbon steel but rather as sorbite. This points to the presence of a certain amount of vanadium in the ferrite and cementite (Fe_3C), an assumption which seems quite logical in view of what was said in the foregoing. The point at which vanadium absorbs the totality of the carbon in the authors' steels (of about eutectoid composition) is about 5 to 6 per cent. vanadium. The composition at which V_4C_3 enters could not be determined.²

The Heat Treatment and Mechanical Properties of Vanadium Steel.—Guillet found the vanadium steels to be so sensitive to heat and mechanical treatment during forging that, in order to get a correct comparison of the various compositions, he determined the mechanical properties of his steels after annealing at 900°C.³ His tests brought out the relatively great influence of vanadium in affecting the properties of steel, particularly in the pearlitic steels, by increasing the elastic limit, tensile strength and hardness, but without materially lowering the ductility and toughness. Vanadium was found to precipitate carbon as annealing carbon, much the same as silicon does.⁴ Quenching from 850°C. converted the pearlite into martensite much the same as in carbon steel, but the effect on the mechanical properties was much more intense. The sensitivity of vanadium steel to forging

¹ *Journ. Iron and Steel Inst.*, 1912, No. 1, p. 215.

² The carbide V_4C_3 dissolves very slowly in molten steel, at least at ordinary refining temperatures, hence in the manufacture of vanadium steel a ferrovanadium with low carbon content must be employed.

³ *Alliages Metalliques*, p. 349.

⁴ The work of HATFIELD on the effect of vanadium on cast iron showed that vanadium evidently tends to keep the carbon in the combined state, due, possibly, to its partial displacement of silicon from the carbide. *Journ. Iron and Steel Inst.*, 1911, No. 1, p. 318.

and mechanical work was shown by the effect of annealing at 900°C. which was not infrequently found to raise the resistance to impact from about 3 kilogram-meters for the forged steel to about 30 kgm.

Pütz¹ verified the work of Guillet in that he found an increase in the tensile strength of 86 per cent. and in the elastic limit of 145 per cent., of forged steel, by the addition of 0.68 per cent. vanadium. This effect did not vary much with the carbon content but was not nearly as intense in annealed steels. He noted the fining effect of vanadium on both the ferrite and pearlite, and found by experiment that the stability of sorbite was greatly increased.

The following table, taken from McWilliams and Barnes, gives the mechanical properties of the ternary vanadium steels, containing the usual amount of vanadium and with varying carbon content.²

It was pointed out in the discussion that the results showed that the 0.09 per cent. carbon steel, as forged, showed an exceptionally high yield point and tensile strength and that tempering certain of the quenched bars at 500°C. produced a stronger steel than tempering at 400°C., and that the necessity for continuing the work on this material was clearly indicated.

Of the simple ternary steels, only those within the pearlite field promise commercial possibilities and we may well say, in the words of Mr. J. Kent Smith that "the well-proven beneficial effect of vanadium on steel was due to at least three causes. First, because vanadium was a unique scavenger in that it removed oxides and nitrides with the resultant formation of fluid and readily separable products, so that the metal was indirectly toughened and put automatically, so to speak, into the very best condition to receive further benefit. Secondly, without doubt a proportion of vanadium went into solid solution under normal conditions in the ferrite of vanadium steel which was much more resistant to wear and to the formation of slip bands than was normal ferrite, while furthermore, as it seemed to oppose the ready passage of carbides through it, the tendency of the vanadium steels was to be highly sorbitic in character. Thirdly, the direct strengthening of the steel seemed to be due to the forma-

¹ *Metallurgie*, 1906, Vol. 3, p. 649 and p. 714.

² *Journ. Iron and Steel Inst.*, 1911, No. 1, p. 294.

TABLE 114.—MECHANICAL PROPERTIES OF VANADIUM STEEL

McWILLIAMS AND BARNES

As Received

Analysis		Yield point, lbs. per sq. in.	Tensile strength, lbs. per sq. in.	Elonga- tion, per cent. on 2 in.	R. A., per cent.	Arnold's altern. stress test
C	V					
0.09	0.16	75,264	85,344	24.0	70.0	249
0.23	0.16	66,304	90,720	23.0	55.1	295
0.40	0.23	87,360	120,288	18.0	41.6	184
0.56	0.21	87,360	133,280	10.5	17.3	171
0.71	0.22	98,560	157,696	13.0	23.3	120
0.98	0.21	87,360	155,904	9.5	17.6	121
1.32	0.20	85,120	148,736	4.5	3.6	51

Annealed

Slowly heated up to 950°C.; held for about 18 hours; cooled in furnace.

0.09	0.16	29,568	51,520	39.0	72.7	328
0.23	0.16	27,776	56,896	37.5	62.2	388
0.40	0.23	36,736	68,992	32.0	39.2	345
0.56	0.21	32,256	78,624	26.0	43.0	248
0.71	0.22	38,080	92,512	20.0	27.9	178
0.98	0.21	35,840	89,824	18.0	27.6	157
1.32	0.20	35,840	84,448	28.0	44.6	211

Quenched from 850°C. in water after 15 min.; drawn at 400°C.

0.09	0.16	41,216	60,704	33.0	78.9	314
0.23	0.16	58,240	85,120	31.5	66.8	341
0.40	0.23	100,800	127,232	18.0	50.5	233
0.56	0.21	114,240	149,184	16.5	44.6	217
0.71	0.22	147,840	186,368	14.0	40.8	175
0.98	0.21	159,488	208,320	11.5	33.5	192
1.32	0.20	170,240	207,648	4.5	9.1	

Quenched from 850°C. in water after 15 min.; drawn at 700°C.

0.09	0.16	44,800	62,944	35.0	74.7	285
0.23	0.16	55,552	79,968	31.0	69.2	256
0.40	0.23	78,848	102,816	26.5	62.0	202
0.56	0.21	80,640	112,448	24.5	57.5	196
0.71	0.22	91,840	126,336	21.0	50.0	201
0.98	0.21	94,080	135,072	19.5	43.8	171
1.32	0.20	89,600	136,416	17.0	35.0	91

tion of complex carbides." Consequently vanadium was an absolutely unique metal.

The steels containing the double carbide were found to be of but little interest (commercially), particularly in view of the high cost of vanadium, and, for a discussion of their properties and behavior, reference will be made to the original. Arnold and Read found that quenching their steel containing 1.07 per cent. carbon and 10.03 per cent. vanadium from 850°C., 1000°C., and 1050°C., produced no appreciable hardening. All, after quenching, were soft to the file. When quenched from above 1300°C. the steel became very hard, even hard enough to strip a file. To date there has been no satisfactory explanation of this effect.

Vanadium in Steel Castings.—The grain of vanadium steel castings, as shown on fracture, is finer than that of ordinary castings and more nearly resembles the grain of annealed steel, although in the unannealed state vanadium steel castings are said to be more brittle than carbon steel castings.¹ Aside from the refining effect of vanadium and its ability to remove residual oxygen, and possibly nitrogen, it increases the tensile strength and resistance to impact as well as the ratio of the elastic limit to the tensile strength, as compared to carbon steel. It is especially beneficial in low carbon low manganese steel. Vanadium in steel castings is said by Norris² to increase their elastic limits by about 30 per cent. and to give 50 per cent. greater resistance to alternating stresses.³ More than 0.2 per cent. vanadium does not seem to be worth while.

Physical Properties.—The electrical properties have been reported by Portevin.⁴ It was found that the resistance increased with the amount of vanadium in solution but that it was practically independent of the amount of free carbide.

Very little has been reported on the magnetic properties of vanadium steel, but vanadium evidently affects the magnetic properties much the same as tungsten and molybdenum do.

¹ CONE, *Iron Age*, 1912, Vol. 90, p. 645.

² American Foundryman's Assoc., 1911, p. 479.

³ Steel for certain large castings analyzing Si 0.25, S 0.04, P 0.05, Mn 0.55–0.60, C 0.26–0.30, gave a tensile strength of 60,000–70,000 lbs., elastic limit 37,000–39,000 lbs., elongation 27 per cent., reduction of area 40 per cent.; when 0.2 per cent. vanadium was added to this steel the castings had a tensile strength of 81,000 lbs. and elastic limit of 45,000 lbs.

⁴ *Rev. de Metallurgie*, 1909, Vol. 6, p. 1340.

Lonsdale¹ examined the magnetic properties of vanadium steel as annealed, quenched, and heat-treated. He found that the permeability is lower in vanadium steel than in other kinds of steel of equal carbon content, and that the hysteresis and coercive force are greater than is given in tables for the principal steels.

Uses.—Vanadium steel, the ternary steel, has a somewhat limited use at present, and then principally for about the same purposes as ordinary steel. When present in amounts up to about 0.2 per cent. vanadium is used largely for its beneficial influence on the static and dynamic properties and for its cleansing effect. These steels make excellent construction steels. When present in amounts up to about 1 per cent. it is used on account of the great increase in hardness produced. These steels are used as tool steel, chisels, punches, etc. The principal use of vanadium is as an addition to other steels, and will be considered in this respect later.

TITANIUM STEEL

It was early found by Guillet² that titanium up to about 9 per cent. evidently has very little effect in improving the properties of steel, although the quenched steels were somewhat more brittle than the carbon steels. A steel with 8.71 per cent. titanium and 0.65 per cent. carbon showed a tensile strength of 167,000 lbs. per sq. in., elastic limit of 88,900 lbs. per sq. in., elongation 8.5 per cent., reduction of area 29.7 per cent., resistance to impact 5 mkg. per sq. cm., and Brinell hardness of 248. The principal use of titanium in iron and steel is as a deoxidizer and cleansing agent.

BORON STEEL

The boron steels do not have any commercial importance and consequently only a brief review of some of the results which have been obtained will be given here. Osmond, in 1890, found that Ar_3 and Ar_2 of pure iron were lowered by the addition of boron whose action is analogous to that of carbon. He found a liberation of heat between 980° and 940° which he said represented the solidification of a small quantity of borate of iron formed by the surface oxidation of the metal.

The influence of boron on steel was reported on a few years later

¹ *Phys. Zeits.*, Vol. 14, p. 581.

² *Genie Civil*, 1904, Vol. 45, p. 327; *Alliages Metall.*, p. 362.

by Moissan and Charpy.¹ A steel with 0.58 per cent. boron, 0.17 per cent. carbon, and 0.30 per cent. manganese showed evolutions of heat at 1140°C., 1040°C., 830°C., 730°C. and 660°C., the last three corresponding to Ar₃, Ar₂, and Ar₁. They assumed, although without justification, that the heat effect at 1140°C. corresponded to Ar₁ in hard steel. This point was found in steels containing as much as 10 per cent. boron. Mechanical tests showed that boron had a very great influence in strengthening steels and that by quenching from 900° to 1100°C. a tensile strength of 185,000 lbs. per sq. in. and an elongation of 3 per cent. were obtained. Inasmuch as the quenched steels could be filed as easily as the annealed steel, it cannot be said that they were hardened by the treatment. Steels with no boron containing 0.37 per cent. carbon when quenched, on the contrary, were hard.

The next systematic investigation was that of Guillet who has submitted a report on his work as a Carnegie Research.² Under the microscope, a new constituent was noticed in the annealed boron steels, a eutectic structure containing ferrite. The special constituent was found to disappear on quenching from high temperatures. The special constituent is said to be a boro-carbide of iron whose composition varies with the percentage of boron and carbon in the steel. Its presence is always injurious to the mechanical properties of the metal.

The mechanical tests given in Table 115, confirm the work of Moissan and Charpy. The steels were found to contain considerable ductility as measured by elongation and contraction of area, but were found to be quite brittle when tested by the notched bar impact test, which Guillet calls a confirmation of the fact that a steel may possess a fair degree of elongation and yet be brittle. Quenching greatly increased the strength and lowered the ductility of even the low carbon steels. It is interesting to note that quenching, by eliminating the special constituent, doubled the resistance to shock while the elongation is only 20 to 25 per cent. that of the forged steel. The quenched steels, containing about 0.2 per cent. carbon, while having fairly high Brinell hardness numbers (311 to 470) could all be very easily worked. The author points out that therefore there is no relation between Brinell hardness number and the degree of

¹ *Compt. Rend.*, 1895, Vol. 120, p. 130.

² *Journ. Iron and Steel Inst.*, 1907, No. 2, p. 207; see also *Compt. Rend.*, 1907, Vol. 144, p. 1049.

workability of the material, a fact which he has brought out in connection with other special steels, principally those containing γ iron.

On the whole, the boron steels possess high tensile strength and elastic limit but at the same time are no more brittle than many steels used in current practice.

TABLE 115.—MICROSTRUCTURE AND MECHANICAL PROPERTIES OF BORON STEEL. GUILLET

Composition		Structure	Tensile tests				Shock test ¹	Hardness No. ²
C	B		T. S., lbs. per sq. in.	E. L., lbs. per sq. in.	Elong., per cent.	R. A., per cent.		
0.180	0.215	Pearlite + traces of special constituent...	53,300	41,500	34.5	57.5	3	110
0.224	0.462	Pearlite.....	56,300	41,500	27.0	55.0	3	105
0.207	0.844	Special constituent.....	85,400	42,300	14.0	26.8	3	161
0.281	1.514	Special constituent.....	73,400	44,800	5.5	4.5	2	200
Second Series								
0.475	0.155	Pearlite and the special constituent.....	72,500	49,000	17.0	27.3	2	145
0.595	0.406	Pearlite and the special constituent.....	76,800	55,470	18.0	22.8	3	159
First Series; Quenched at 850°C.								
0.180	0.215	Martensite.....	97,400	81,071	7.5	36.5	6	336
0.224	0.464	Martensite + traces of special constituent...	209,700	142,232	6.5	30.6	6	311
0.207	0.844	Martensite and special constituent.....	248,900	184,900	4.0	10.6	6	470
0.281	1.514	Martensite and special constituent.....	170,678	179,200	1.0	3	447
Second Series; Quenched at 775°C.								
0.475	0.155	Martensite + traces of special constituent...	Broke badly				3	558
0.595	0.406	Martensite + traces of special constituent...	Broke badly				1	652

¹ Fremont test pieces with a Guillery falling weight.

² Pressure = 3000 kgs.; diam. of ball 10 mm.

Hannesen found a eutectic between iron and Fe_3B_2 ¹ at 4 per cent. boron and 1170°C. which is probably the eutectic noted by earlier experimenters.² The compound Fe_3B_2 was found to have a melting point of 1321°C., and to be extremely hard. Both A_3 and A_2 were lowered by the addition of boron. From this work it would appear that the special constituent of Guillet is the compound Fe_3B_2 containing more or less carbon, and that the eutectic is a mixture of ferrite and this compound. In the pure iron-boron alloys the eutectic was found to occur down to about 0.25 per cent. boron.

Tschischewsky and Herdt³ redetermined the eutectic at 3.1 per cent. boron, the constituents being ferrite with 0.08 per cent. boron in solution and Fe_2B , instead of Fe_3B_2 . They also found that boron makes the alloys extremely brittle and fragile.

From a report from the electrochemical works, Bitterfeld,⁴ the field of boron steels does not seem to be very encouraging due principally to red shortness and brittleness.

Steels containing boron must be worked at a red heat inasmuch as they are extremely tender at temperatures above 1000°C.⁵

The Magnetic Properties.—The magnetic properties of two high carbon steels, containing 0.5 and 0.8 per cent. boron, were determined by Curie,⁶ but little difference was found between boron steel and carbon steel. The magnetic properties of carbonless iron-boron alloys have recently been determined by Yensen.⁷ Summarizing, the first effect of boron is to reduce iron oxide, by which action it benefits the iron slightly. Boron added in excess of this amount alloys with the iron and becomes detrimental to the magnetic properties. The specific electrical resistance of iron is increased by 0.62 microhms per 0.1 per cent. boron while the elastic limit and tensile strength are slightly raised.

From this it is quite evident why the boron steels have so far found no commercial application.

Other ternary steels have been examined but the results have

¹ This may be the Fe_2B of JASSONEUX, *Compt. Rend.*, 1907, Vol. 145, pp. 121 and 195.

² *Zeit. anorg. Chemie.*, 1914, Vol. 89, p. 257.

³ See *Iron Age*, 1916, Vol. 98, p. 396.

⁴ *Stahl u. Eisen*, 1914, Vol. 34, p. 1530.

⁵ Woodward, Personal communication.

⁶ *Bull. Soc. d'Encour.*, 1898, p. 53.

⁷ *Bull. No. 77*, Engineering Expt. Station, University of Illinois, March, 1915.

so far been of little practical interest and consequently only a bibliography will be given here.

Tantalum Steel

GUILLET, *Compt. Rend.*, 1907, Vol. 145, p. 327.

PORTEVIN, Iron and Steel Inst., Carnegie Scholarship *Memoirs*, 1909, Vol. 1, p. 231.

MESSRS. BLACKWELL and SONS, *Iron and Coal Trades Review*, 1909, Vol. 78, p. 933 and p. 937.

Iridium Steel

BECKER, "High Speed Steel," p. 43.

Tin Steel

GUILLET, *Compt. Rend.*, 1905, Vol. 140, p. 1689.

GUILLET, *Rev. de Metallurgie*, 1904, p. 500; also *Genie Civil*, 1904, Vol. 45, p. 327.

GOERENS and ELLINGEN, *Metallurgie*, 1910, Vol. 7, p. 72-79.

COMPLEX CONSTRUCTION STEELS

It has been found advantageous, to secure steels for special purposes, to add two or at times even more elements to steel. In this way one element will reinforce the other element and produce a combined effect which is, many times, much better than could be secured by addition of either of the elements alone. In certain cases the advantages of adding each of the elements are secured without necessarily introducing the disadvantages. The number of combinations of this kind which are in actual use at present is, of course, limited and here we shall consider the chrome-nickel steels and the chrome-vanadium steels, which are the two leading quaternary steels, and the complex molybdenum steels, which show promise.

THE CHROME-NICKEL STEELS

The chrome-nickel steels were first described by Guillet in 1905 in a paper on the steels used for motor car construction in France.¹ He stated at that time that the advantages derived from nickel steels are again found in the chrome-nickel steels but

¹ *Journ. Iron and Steel Inst.*, 1905, No. 2, p. 185.

that the mineralogical hardness on quenching is increased by the addition of chromium. This produces a steel which is considerably better than nickel steel in case the parts are subjected to wear. The next year, in a monumental treatise on Quaternary Steels, Guillet again described the chrome-nickel steels.¹ In this paper, the properties of steels of a very wide range in composition were reported. He concluded that only the pearlitic and polyhedral steels could be used commercially, but that, of course, the cost of the polyhedral steels would limit their use. The effect of the first addition of chromium to pearlitic nickel steel is to decrease the grain size, and to make the steels more sorbitic. This fining effect, it may be assumed, tends to overcome the slight embrittling effect which might be caused by the chromium. Further additions, depending upon the sum of the carbon, nickel and chromium, give a martensitic structure. These martensitic steels are commonly referred to as "air hardening" steels.

Chrome-nickel steel of the ordinary commercial grade used in automobile construction can be sufficiently softened by annealing for machining and yet, at the same time, the steel can be heat treated to produce great strength and hardness. Annealing is carried on in the usual manner by heating up slowly to just above A_{c3} , holding at the temperature sufficiently long to produce uniform and chemically homogeneous austenite, and cooling slowly. The rate of transformation and diffusion is slower than for carbon steel, as is generally the case with special steels. To assist in the annealing operation, if not too expensive, the steel may be given a preliminary quench from 75 to 100°C. over the critical range before annealing. Again, the steel may be annealed or softened sufficiently by heating up to just below the critical range, which, when it follows a quench, also puts the steel in an excellent condition for machining and subsequent quenching.

For our purposes we may classify the chrome-nickel steels into three types which contain the following percentages of nickel and chromium (1) nickel 1.5, chromium 0.7; (2) nickel 3.0, chromium 0.6–0.9; (3) nickel 3.5, chromium 1.5. Each type is used generally with three different carbon contents: (a) low carbon for case hardening parts; (b) 0.35 carbon for shafting and similar parts; and (c) 0.50 carbon for heat treated gears, crankshafts, and transmission lines of automobiles, motor trucks, etc. The critical points of these three grades of steels, as de-

¹ *Ibid.*, 1906, No. 2, p. 37.

terminated by the Bureau of Research of the Midvale Steel Company, are given in the following figures. The correct temperature for the final quench would be about 25°C. above the upper line.

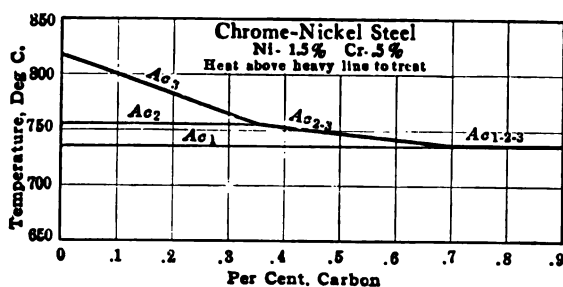


FIG. 137.—Critical points of chrome-nickel steel. (Midvale Steel Co.)

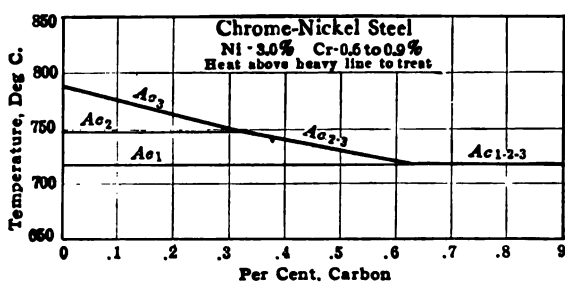


FIG. 138.—Critical points of chrome-nickel steel. (Midvale Steel Co.)

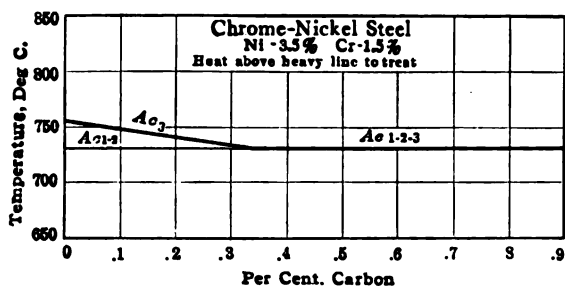


FIG. 139.—Critical points of chrome-nickel steel. (Midvale Steel Co.)

The results which have been obtained with some of these steels are given in the following tables, along with the heat treatments used.

TABLE 116.—MECHANICAL PROPERTIES OF CHROME-NICKEL STEELS
I. (a) Type composition C 0.20, Ni 1.5, Cr 0.7, Mn 0.4.

Critical Points. Ac_1 725°C.; Ac_2 750°C.; Ac_3 790°C.; Ar_{32} 730°C.;
 Ar_1 645°C.

"Fibreing" treatment, 870°C.— $\frac{1}{2}$ hr.—Oil 1 in. round bar.

815°C.— $\frac{1}{2}$ hr.—Oil 1 in. round bar.

650°C.— $\frac{1}{2}$ hr.—Lime 1 in. round bar.

Quenching treatment, 815°C.— $\frac{1}{2}$ hr.—Oil $\frac{1}{2}$ in. round bar.

Drawing temperature	Tensile strength, lb. per sq. in.	Elastic limit, ¹ lb. per sq. in.	Elongation, per cent.	R. A., per cent.
Not drawn.....	110,500	?	16	47
205°C. 1 hr.....	117,000	100,000	15	60
315°C. 1 hr.....	116,000	98,000	14	62
425°C. 1 hr.....	104,000	78,000	20	68
540°C. $\frac{1}{2}$ hr.....	95,000	70,000	24	70
650°C. $\frac{1}{2}$ hr.....	80,000	56,000	30	74

¹ Elastic limit of bars drawn at 315°C. and below taken by drop of beam; of those drawn at 425°C. and above, by extensometer.

I. (b) Type composition, C 0.30; Ni 1.5; Cr 0.7; Mn 0.4.

Critical Points. Ac_1 725°C.; Ac_{23} 750°C.; Ar_{32} 700°C.; Ar_1 655°C.

"Fibreing" treatment, 870°C.— $\frac{1}{2}$ hr.—Oil 1 in. round bar.

775°C.— $\frac{1}{2}$ hr.—Oil 1 in. round bar.

650°C.— $\frac{1}{2}$ hr.—Lime 1 in. round bar.

Quenching treatment, 775°C.— $\frac{1}{2}$ hr.—Oil $\frac{1}{2}$ in. round bar.

Drawing temperature	Tensile strength, lb. per sq. in.	Elastic limit, lb. per sq. in.	Elongation, per cent.	R. A., per cent.
Not drawn.....	224,000	210,000	4	10
205°C. 1 hr.....	220,000	220,000	6	20
315°C. 1 hr.....	204,000	200,000	9	40
425°C. 1 hr.....	173,000	138,000	13	55
540°C. $\frac{1}{2}$ hr.....	135,000	105,000	17	60

THE SPECIAL STEELS

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I. (c) Type composition, C 0.50, Ni 1.5, Cr 0.7, Mn 0.4.

Critical Points. Ac 730°C.; Ar 560°C.

"Fibreing" treatment, 870°C.—½ hr.—Oil 1 in. round bar.

770°C.—½ hr.—Oil 1 in. round bar.

650°C.—½ hr.—Lime 1 in. round bar.

Quenching treatment, 770°C.—½ hr.—Oil 1 in. round bar.

Drawing temperature	Tensile strength, lb. per sq. in.	Elastic limit, lb. per sq. in.	Elongation, per cent.	R. A., per cent.
Not drawn.....	200,000			
205°C. 1 hr.....	296,000	288,000	2	3
315°C. 1 hr.....	273,000	248,000	9	40
425°C. 1 hr.....	220,000	202,000	11	47
540°C. ½ hr.....	192,000	175,000	13	50
650°C. ½ hr.....	158,000	142,000	17	58

II. (a) Type composition, C 0.18, Ni 3.0, Cr 0.70, Mn 0.40.

Critical Points, Ac₁ 715°C.; Ac₂ 745°C.; Ac₃ 760°C.

"Fibreing" treatment,

Quenched 870°C.—½ hr.—Oil ½ in. round bar.

Quenched 800°C.—½ hr.—Water ½ in. round bar.

Drawing temperature	Tensile strength, lb. per sq. in.	Elastic limit, lb. per sq. in.	Elongation, per cent.	R. A., per cent.	B. H. No.	S. H. No.
Not drawn.....	196,000	180,000	10	36	400	60
205°C. 1 hr.....	183,000	170,000	14	52	375	57
315°C. 1 hr.....	176,000	162,000	15	54	360	55
425°C. 1 hr.....	160,000	145,000	17	57	325	52
540°C. ½ hr.....	135,000	119,000	18	60	275	48
650°C. ½ hr.....	108,000	90,000	22	65	200	43

II. (b) Type composition, C 0.30, Ni 3.0, Cr 0.70, Mn 0.50.

Critical Points. Ac_{32} 725°C.; Ac_1 710°C.; Ar_{32} 620°C.; Ar_1 525°C."Fibreing" treatment, 870°C.— $\frac{1}{2}$ hr.—Oil 1 in. round bar.760°C.— $\frac{1}{2}$ hr.—Oil 1 in. round bar.650°C.— $\frac{1}{2}$ hr.—Lime 1 in. round bar.760°C.— $\frac{1}{2}$ hr.—Oil 1 in. round bar.

Drawing temperature	Tensile strength, lb. per sq. in.	Elastic limit, lb. per sq. in.	Elongation, per cent.	R. A., per cent.
Not drawn.....	268,000	202,000	8	25
205°C. 1 hr.....	240,000	222,000	12	46
315°C. 1 hr.....	195,000	184,000	14	56
425°C. 1 hr.....	148,000	138,000	19	62
540°C. $\frac{1}{2}$ hr.....	129,000	110,000	21	64
650°C. $\frac{1}{2}$ hr.....	120,000	95,000	22	62

II. (c) Type composition, C 0.45, Ni 3.0, Cr 0.70, Mn 0.50

Critical Points. Ac 710°C.; Ar 620°C."Fibreing" treatment, 870°C.— $\frac{1}{2}$ hr.—Oil 1 in. round bar.760°C.— $\frac{1}{2}$ hr.—Oil 1 in. round bar.650°C.— $\frac{1}{2}$ hr.—Lime 1 in. round bar.760°C.— $\frac{1}{2}$ hr.—Oil 1 in. round bar.

Drawing temperature	Tensile strength, lb. per sq. in.	Elastic limit, lb. per sq. in.	Elongation, per cent.	R. A., per cent.	B. H. No.	S. H. No.
Not drawn.....	228,000					
205°C. 1 hr.....	275,000	270,000	10	38	500	77
315°C. 1 hr.....	230,000	205,000	12	48	450	73
425°C. 1 hr.....	190,000	170,000	14	54	380	65
540°C. $\frac{1}{2}$ hr.....	160,000	135,000	16	56	325	55
650°C. $\frac{1}{2}$ hr.....	130,000	110,000	22	61	275	47

III. (a) Type composition, C 0.12, Ni 3.5, Cr 1.5, Mn 0.40.

Critical Points. A_{c1} 730°C.; A_{c2} 745°C.Quenched 870°C.— $\frac{1}{2}$ hr.—Oil $\frac{1}{2}$ in. round bar.790°C.— $\frac{1}{2}$ hr.—Water $\frac{1}{2}$ in. round bar.

Drawing temperature	Tensile strength, lb. per sq. in.	Elastic limit, lb. per sq. in.	Elongation, per cent.	R. A., per cent.	B. H. No.	S. H. No.
Not drawn	190,000	160,000	13	42	365	54
205°C. 1 hr.	176,000	160,000	16	56	340	53
315°C. 1 hr.	166,000	150,000	17	60	325	51
425°C. 1 hr.	150,000	130,000	18	64	300	49
540°C. $\frac{1}{2}$ hr.	120,000	104,000	20	68	237	45
650°C. $\frac{1}{2}$ hr.	102,000	88,000	25	72	200	40

III. (b) Type composition, C 0.3, Ni 3.5, Cr 1.5, Mn 0.40.

Critical Points. A_c 740°C.; A_r 455°C."Fibreing" treatment, 870°C.— $\frac{1}{2}$ hr.—Oil 1 in. round bar.760°C.— $\frac{1}{2}$ hr.—Oil 1 in. round bar.650°C.— $\frac{1}{2}$ hr.—Lime 1 in. round bar.760°C.— $\frac{1}{2}$ hr.—Oil 1 in. round bar.

Drawing temperature	Tensile strength, lb. per sq. in.	Elastic limit, lb. per sq. in.	Elongation, per cent.	R. A., per cent.
Not drawn	260,000	240,000	10	34
205°C. 1 hr.	240,000	222,000	12	44
315°C. 1 hr.	210,000	190,000	13	53
425°C. 1 hr.	188,000	168,000	14	56
540°C. $\frac{1}{2}$ hr.	132,000	112,000	18	64
650°C. $\frac{1}{2}$ hr.	120,000	100,000	22	70

E. L.—Proportional limit by extensometer.

Elongation measured on two inches.

Reproduced by courtesy of the Midvale Steel Company.

Some recent results obtained with chrome-nickel steels, including results of the notched bar impact test, are reproduced in Table 117. These figures were kindly supplied by the Bureau of Research, Midvale Steel Company.

TABLE 117.—MECHANICAL PROPERTIES OF CHROME-NICKEL STEEL
Steel. C 0.33; Mn 0.45; P 0.023; S 0.025; Si 0.192; Ni 2.77; Cr 0.74
Final treatment; 1400°F.— $\frac{1}{2}$ hr.—Oil

Drawn	Tensile strength	Elastic limit	Elongation	R. A.	Izod
1100°F.— $\frac{1}{2}$ hr.—Oil.....	126,000	100,000	21.5	64.0	17.0
1200°F.— $\frac{1}{2}$ hr.—Oil.....	119,500	97,000	22.5	65.0	18.6

Steel. C 0.33; Mn 0.44; P 0.019; S 0.025; Si 0.199; Ni 3.50; Cr 1.78
Final treatment; 1425°F.— $\frac{1}{2}$ hr.—Oil

Drawn	Tensile strength	Elastic limit	Elongation	R. A.	Izod
1100°F.— $\frac{1}{2}$ hr.—Oil.....	144,000	117,500	19.5	62.0	13.6
1200°F.— $\frac{1}{2}$ hr.—Oil.....	133,500	110,000	21.0	64.5	18.0

Steel. C 0.52; Mn 0.56; P 0.038; S 0.020; Si 0.14; Ni 2.88; Cr 0.81
Final treatment; 1400°F.— $\frac{1}{2}$ hr.—Oil

Drawn	Tensile strength	Elastic limit	Elongation	R. A.	Izod
1100°F.— $\frac{1}{2}$ hr.—Oil.....	154,500	130,000	17.5	54.1	9.8
1200°F.— $\frac{1}{2}$ hr.—Oil.....	137,500	115,000	20.3	58.6	13.8

Steel. C 0.49; Mn 0.45; P 0.019; S 0.018; Si 0.19; Ni 3.61; Cr 1.30
Final treatment; 1425°F.— $\frac{1}{2}$ hr.—Oil

Drawn	Tensile strength	Elastic limit	Elongation	R. A.	Izod
1100°F.— $\frac{1}{2}$ hr.—Oil.....	157,500	135,000	15.5	50.6	12.4
1200°F.— $\frac{1}{2}$ hr.—Oil.....	142,000	110,000	19.0	57.3	14.9

Material used: Rolled bars, 1 inch square. Bars were annealed and quenched, 1600°F.— $\frac{1}{2}$ hr.—Oil, and then treated as given. Standard tensile test specimens were used. Izod figures are in foot-pounds, obtained with specimens $\frac{3}{8}$ in. \times $\frac{3}{16}$ in. with a 90° V nick, 0.05 in. deep.

Temper Brittleness in Chrome-Nickel Steels.—It will be noted that the chrome-nickel steels in the preceding table were quenched in oil after drawing at the temperatures 1100° and 1200° F., or 593° and 650°C. In this respect the heat treatment of the chrome-nickel steels differs radically from that of the straight

carbon steels as the latter are slowly cooled from the drawing temperature and with satisfactory results. This final quench is used in order to put the steels in their toughest condition and slow cooling from the final draw would allow the steels to change to a much more brittle condition. This latter phenomenon has been called "temper brittleness" and occurs to a greater or lesser degree in nickel steels, chrome-vanadium steels and even in carbon steels (Rogers). The importance of this effect has only recently been recognized due, possibly, to the fact that (notch) brittleness in these steels is not at all shown by the usual tensile test. The notched bar impact test brings out the vast difference between slow cooling and rapid cooling from the drawing temperature and again demonstrates its worth as an adjunct of the tensile test.

The following figures are cited to show temper brittleness in a steel analyzing C 0.24; Si 0.20; Mn 0.49; S 0.029; P 0.022; Ni 3.54; Cr 0.59.

TABLE 118.—TEMPER BRITTLNESS IN CHROME-NICKEL STEEL. GREAVES

No.	How cooled	Elastic limit	Yield point	Tensile strength	Elongation	R. A.	Brinell	Impact figure
1	Quench ..	49,000	73,500	102,000	23.5	49	221	73
2	Slow cool	60,500	73,500	99,500	25.5	55	215	35
3	Quench ..	67,000	87,500	116,000	17	34	247	70
4	Slow cool	62,500	84,000	110,500	19	39	234	12

1 and 2 were quenched in water from 850°C. and tempered at 675°C. for 8¼ hours; 1 was then quenched in water and 2 was allowed to cool slowly, 3 and 4 were quenched in oil from 1000°C. and tempered at 670°C. for 2 hours; 3 was then quenched in water and 4 was allowed to cool slowly. The E. L., Y. P., and T. S. are in pounds per square inch and the elongation and reduction of area were measured with a two inch test bar, 0.564 inch in diameter. The impact figures are approximate Izod figures calculated from results obtained with the Guillery machine.

As a result of his investigation, Greaves drew the following conclusions regarding temper brittleness. (1) Wide differences in the impact figure (notch toughness) with almost identical tensile properties can be produced by suitable heat treatment. (2) Steels of almost identical composition may vary in the degree of brittleness produced by identical treatment. (3) The impact figure after slow cooling from the tempering temperature is lower, the higher the initial quenching, or hardening, tempera-

ture. (4) Reheating to a temperature of ca. 520°C. results in brittleness, whatever the subsequent rate of cooling may be. (5) Brittle steel (temper brittleness) can be restored (toughened) by reheating to between 600° and 670°C. and cooling rapidly. (6) The results are in accordance with the assumption of a critical temperature range in the vicinity of 550°C., above which the tough condition is stable and below, the brittle condition.¹

It might be expected that such a marked difference in toughness would be coincident with a pronounced change in microstructure, but such is not the case. Both conditions show the typical sorbitic structure. To the writer's knowledge the only other means of distinguishing readily between these two conditions is by magnetic analysis. It is true that a fracture test shows the tough steels to possess "fibre" as contrasted with the uniform, fine-grained appearance of the brittle steels.

The rate of cooling from the tempering temperature (through the critical range at about 550°C.) has an effect on the toughness of the steel, as is shown by the following figures due to Wood and Archer.²

TABLE 119.—RATE OF COOLING AND TEMPER BRITTLENESS

Manner of cooling	Isod impact value
Water quenched.....	50.0
Oil quenched.....	48.0
Air cooled.....	43.0
Furnace cooled.....	8.7

This effect is in harmony with the assumption of a critical point in the neighborhood of Greaves' critical range, as has been advanced by Rogers.³ This critical point is supposed to correspond to a re-resolution of the carbides. The effect of the rate of cooling from above this temperature is obvious. It is understood that not all steels of this type show the temper brittleness described here.⁴

Chrome-nickel steels were discussed by Longmuir in his paper on high-tension steels,⁵ but there was little original information given. It was brought out that both nickel and chrome-nickel

¹ GREAVES, *Journ. Iron and Steel Inst.*, 1919, No. 2, p. 329.

² JEFFRIES, *Bull. Amer. Inst. M. and M. Eng.*, No. 158, Sect. 20.

³ ROGERS, *Journ. Iron and Steel Inst.*, 1919, No. 2, p. 325.

⁴ BREARLEY, *Journ. Inst. Auto. Eng.*, 1916-17, Vol. 11, p. 347; PHILPOT., *Ibid.*, 1917-18, Vol. 12, p. 235; HATFIELD, *Proc. Inst. Mech. Eng.*, May, 1919; HAYWARD, *Chem. and Met. Eng.*, 1919, Vol. 21, p. 519.

⁵ *Journ. Iron and Steel Inst.*, 1909, No. 1, p. 383.

steel forgings were produced with an elastic limit of 90,000 to 112,000 lbs., a tensile strength of 112,000 to 134,500 lbs. per sq. in., and an elongation of 25 to 20 per cent. on 2 inches. One test was cited which gave an elastic limit of 147,840 lbs., a tensile strength of 166,656 lbs., and an elongation of 20 per cent.

In general the chrome-nickel steels are very similar to the nickel steels but (a) they have higher elastic limits with about the same ductility; (b) they are harder than the nickel steels, especially when heat treated; (c) they are more susceptible to heat treatment, and many of them harden considerably when cooled in the air; and (d) they possess dynamic toughness and resistance to fatiguing stresses, when properly treated, in the highest degree and on account of these properties they are not surpassed, as construction steels, by any other steels. It is interesting to note that the static properties of the low nickel, low chromium steels are nearly the same as those of the high nickel, high chromium steels. However the latter type is generally to be preferred for parts which are subjected to exceptionally severe service.

The low chrome-nickel steels are less expensive than either the high chrome-nickel steels or the $3\frac{1}{2}$ per cent. nickel steel and are, therefore, very generally used in sections up to one and one half inch round for parts which require high static properties but which do not require all that can be given in toughness and dynamic properties. They may be readily heat treated to give the following properties:—tensile strength 130,000 lbs., elastic limit 105,000 lbs., elongation 16 per cent., reduction of area 52 per cent., Brinell hardness 275, scleroscope hardness 47; or tensile strength 220,000 lbs., elastic limit 185,000 lbs., elongation 9 per cent., reduction of area 30 per cent., Brinell hardness 390, scleroscope hardness 62.¹

CHROME-VANADIUM STEEL

The first detailed investigation of the properties and heat treatment of chrome-vanadium steel as it is used today, was that of Sankey and Smith in 1904.^{2,3} The material experimented with contained from 0.20 to 0.45 per cent. carbon, about 1 per

¹ Ninth Report, Iron and Steel Division, Soc. Auto. Engineers, August, 1916.

² *Proceed. Inst. Mech. Engineers*, 1904, Pt. 4, p. 1235.

³ Considerable chrome-vanadium steel is sold at present under the name of "vanadium steel."

cent. chromium and about 0.16 per cent. vanadium. This paper was very complete in its description of this steel and brought out the remarkable effect of adding 0.16 to 0.20 per cent. vanadium to a 1 per cent. chromium steel. This may be said to mark the introduction of the chrome-vanadium steels and since that time a large amount of this steel has been used for high grade forgings. They now rank with the chrome-nickel and chrome-nickel-vanadium steels as the most useful of the complex construction steels.

The critical points of the various grades of chrome-vanadium steel have not been published in detail, but in all probability there is a high critical point about 70°C. above the A_{cs} , running from about 940°C. for no carbon to 765°C. at 0.65 per cent. carbon ($A_{C_{123}}$) for steel with 1 per cent. chromium and 0.16–0.20 per cent. vanadium. This point is made evident both by accurate thermal analysis and by the high quenching temperature required to bring out the best properties.¹

The Heat Treatment and Mechanical Properties of Chrome-Vanadium Steels.—The following table is due to Mr. Kent Smith, as communicated by Mr. Harbord.²

TABLE 120.—MECHANICAL PROPERTIES OF CHROME-VANADIUM STEEL

Material	Properties			
	Yield point	Ultimate stress	Elongation, per cent. on 2 in.	R. A., per cent.
	lbs., sq. in.			
Crucible steels (C, 0.22–0.25 per cent.):				
A plain carbon.....	35,840	60,480	35.0	60.0
B plain carbon + 0.5 per cent. Cr.....	51,296	76,160	33.0	60.6
C plain carbon + 1.0 per cent. Cr.....	56,000	85,568	30.0	57.3
D plain carbon + 0.1 per cent. V.....	63,840	77,950	31.0	60.0
E plain carbon + 0.15 per cent. V.....	68,096	81,700	26.0	59.0
F plain carbon + 0.25 per cent. V.....	76,384	88,032	24.0	59.0
G plain carbon + 1.0 per cent. Cr + 0.15 per cent. V.....	81,088	108,804	24.0	56.6
H plain carbon + 1.0 per cent. Cr + 0.25 per cent. V.....	110,656	135,296	18.5	46.3
I nickel steel.....	58,240	94,080	24.0	50.0
K nickel steel + 0.2 per cent. V.....	116,704	129,696	20.5	52.4
Open hearth steels (C, 0.25–0.27 per cent.):				
L plain carbon.....	39,648	72,128	34.0	52.6
M plain carbon + 1.0 per cent. Cr + 0.15 per cent. V.....	77,056	117,824	25.0	55.5

¹ The presence of these high critical points militates against the use of this material for many purposes, such as large forgings, on account of the extra wear and tear on the heat treating furnaces.

² Metallurgy of Steel, p. 424.

This table shows the effect of vanadium in raising the yield point of both carbon and chromium steel without too seriously impairing the ductility. Guillet in his paper on the use of vanadium in metallurgy failed to consider the chrome-vanadium steels, but this was compensated to some extent by the discussions especially that of Mr. Smith.¹ At another place, the question of vanadium as a steel making element was discussed by Smith who took up, in particular, the different types of chrome-vanadium steels.²

The properties of chrome-vanadium steel are very thoroughly given in a booklet "Vanadium Steels" issued by the American Vanadium Company, from which the following results have been taken. The steels are grouped as types, according to the use for which the steel is intended. Characteristics of the Type A steel, in one-inch round bars, quenched in oil from 900°C. and tempered at 600°C. are as follows:

TABLE 121.—PROPERTIES OF CHROME-VANADIUM STEEL

	Mild, per cent.	Regular, per cent.	Full, per cent.
Carbon.....	.18 to .25	.25 to .32	.32 to .40
Manganese.....	.35 to .50	.40 to .60	.40 to .60
Chromium.....	.60 to .80	.80 to 1.00	.80 to 1.00
Vanadium.....	over .16	over .16	over .16

Properties			
	Mild	Regular	Full
Elastic limit, lbs. per sq. in.....	112,000	132,500	146,500
Tensile strength, lbs. per sq. in.....	137,000	149,500	167,500
Elongation in two inches, per cent.....	20	17.5	16.0
Reduction of area, per cent.....	61	58.6	54.5
Hardness number—Brinell.....	277	321	340
Hardness number—scleroscope.....	42	46	49
Alternating impacts, $\frac{3}{8}$ inch throw (Arnold number).....	1250	978	866

NOTE: This Arnold number is not numerically comparable with other numbers given in this text.

¹ *Journ. Iron and Steel Inst.*, 1905, No. 2, p. 115.

² *Journ. Soc. Chem. Ind.*, 1906, Vol. 25, p. 291.

The mild grade is used for case hardened parts, especially case hardened clash gears, and when treated (reheat to 900°C.—oil quench—reheat to 825°C.—water quench—temper at 200°C.) gives 180,000 lbs. elastic limit, 200,000 lbs. tensile strength, elongation 8 per cent., and reduction of area 25 per cent. The regular grade is used for forged parts of automobiles, etc., while the full grade is used for locomotive parts, and transmission parts. The latter is heat treated to give, as locomotive forgings, an elastic limit of 80,000 lbs. and an elongation of 20 per cent. This is just twice the yield point required for carbon forgings for the same elongation.

Type D chrome-vanadium steel is designed primarily for use as springs. It contains more carbon, manganese and chromium than Type A and is therefore stronger but less ductile. It is also used for gears in constant mesh, and the mild grade (C.35 to .45) as rear axle shafts and parts required to resist torsional strains. The high carbon grade is used as tool steel. When heat treated for spring temper (quench 900°C.—oil; temper at 400–450°C. for 20 min.) it is said to have the following characteristics:

Elastic limit, lbs. per sq. in.....	170,000 to 225,000
Tensile strength, lbs. per sq. in.....	190,000 to 250,000
Elongation on 2 inches.....	10 to 15 per cent.
Reduction of area.....	35 to 45 per cent
Brinell hardness.....	418
Scleroscope hardness.....	52
Arnold number, $\frac{3}{8}$ in. throw.....	650 alterations.

When heat treated for gears it has an elastic limit of 200,000 to 230,000 lbs. per sq. in., an elongation of 8 to 12 per cent., Brinell hardness number of 425–555 and scleroscope hardness number of 60–69. This grade contains 0.52 to 0.60 per cent. carbon, 0.60–0.80 per cent. manganese, 0.80–1.10 per cent. chromium, and over 0.16 per cent. vanadium.

Type E is to be used principally as case hardened clash gears as it contains 0.25–0.40 per cent. manganese, 0.25–0.40 per cent. chromium, over 0.12 per cent. vanadium and low carbon. The core of a case hardened part showed 70,000 lbs. elastic limit, 97,000 lbs. tensile strength, 21 per cent. elongation and 62 per cent. reduction of area.

Type G is intended for rolled wheels and tires. It is very similar to D, with high carbon, and also makes a good tool steel.

Heat treated tires (quench in oil from 900°C.; temper at 600°C.) of this steel (C = 0.55–0.65 per cent.) has the following properties:

Elastic limit, lbs. per sq. in.....	130,000
Tensile strength, lbs. per sq. in.....	165,000
Elongation, per cent. on 2 inches.....	14
Reduction of area, per cent.....	40
Brinell hardness number.....	340
Scleroscope hardness number.....	50
Arnold number, $\frac{3}{8}$ inch throw.....	900 alternations

Type H contains C 0.75–0.85 per cent. or 0.85–1.00 per cent. and is used especially for tools. Type J is regular carbon steel for castings to which is added the usual amount of vanadium—0.16 to 0.20 per cent. Tests are cited showing the advantage of adding the vanadium to steel for locomotive frames, *i.e.*, the elastic limit is raised from 36,700 lbs. to 42,600 lbs. and the number of alternating impacts ($\frac{1}{4}$ " throw) from 1918 to 2952. Tests are also cited showing the advantage of adding vanadium to chrome-nickel steel. This steel is said to be well suited for eye-bars for bridge work.¹

¹ Miscellaneous tests of chrome-vanadium steel are as follows:

Chrome-vanadium steel	Elastic limit, lb. per sq. in.	Tensile strength, lb. per sq. in.	Elongation, per cent. 2 in.	R. A., per cent.
Heat treated Type A vanadium steel locomotive side rods, bent cold.....	76,000 to 96,000	100,000 to 125,000	20 to 25	60 to 69
Twisted connecting rods and crankshaft Type A vanadium steel.....	97,000	134,000	21	57.3
Heat treated Type A vanadium steel locomotive main driving axle, 10 in. diam. bent cold without fracture.....	75,000	100,000	20	45
Type J vanadium cast steel main frame for consolidation locomotives, weight 12,900 lbs.	47,130	81,580	30.5	47.9
Type J vanadium cast steel bed plate for upsetting machine, weight 12,900 lbs.	45,990	79,840	27.5	51.4
Destruction test on full-sized eye bar of vanadium steel.....	80,840	99,890	52.3
Elong. in 12 in. = 32.5 %				
Elong. in 20 ft. = 7.9 %				
Tests made from the disc cut out in making the eye or pin hole of the bar gave these properties.....	83,040	94,140	25	71.9
Altern. impacts $\frac{3}{8}$ in. throw = 850.				

The following tests were obtained by the Midvale Steel Co. on steel with 1 per cent. chromium, 0.18 per cent. vanadium and 0.60 per cent. manganese.¹

¹ Quenching temperatures conform to the high A_c point and not to the ordinary A_{c1} point.

TABLE 122.—PROPERTIES OF CHROME-VANADIUM STEEL

Carbon = 0.30 per cent.

Treatment: 900°C.—½ hr.—Oil, Bars ½ in. round.

Critical temperatures: Ac₁ 775°C.; Ac₂₂ 810°C.; Ar₁ 715°C.; Ar₂₂ 760°C.

Drawing temperature	Tensile strength, lbs. per sq. in.	Elastic limit, lbs. per sq. in.	Elongation, per cent. 2 in.	R. A., per cent.	B. H. No.	S. H. No.
Not drawn.....	214,000	1	6		
205°C.....	245,000	230,000	6	20	410	62
315°C.....	236,000	227,000	8	43	405	61
425°C.....	211,000	180,000	11	48	365	55
540°C.....	162,500	142,500	16	53	315	50
650°C.....	149,000	130,000	18	60	285	48

Carbon = 0.40 per cent.

Treatment: 900°C.—½ hr.—Oil, Bars ½ in. round.

Critical temperatures: Ac₁ 770°C.; Ac₂₂ 800°C.; Ar₁ 715°C.; Ar₂₂ 730°C.

Not drawn.....	197,000	0.5	3		
205°C.....	252,000	232,000	1	5	475	72
315°C.....	255,000	250,000	6	27	450	66
425°C.....	226,000	200,000	10	45	390	62
540°C.....	170,000	145,000	14	50	340	56
650°C.....	153,500	137,500	16	56	295	50

Carbon = 0.50 per cent.

Treatment: 900° C.—½ hr.—Oil, Bars ½ in. round.

Critical temperatures: Ac₁ 770°C.; Ac₂₂ 785°C.; Ar₁ 715°C.; Ar₂₂ 720°C.

Not drawn.....	187,500				
205°C.....	258,000	0.5	3		
315°C.....	267,000	240,000	6	27		
425°C.....	238,000	207,500	9	43		
540°C.....	170,000	152,500	14	49		
650°C.....	158,000	140,000	16	54		

COMPLEX MOLYBDENUM STEEL

The latest development in forging and construction steels is that of the complex molybdenum steels. These were developed during the war to meet the demand for light armor plate and high grade forgings. Some of the best Liberty motor crank shafts were made of a chrome-nickel steel to which about 0.5

per cent. molybdenum had been added while a similar grade was used successfully for light armor plate. In the opinion of some metallurgists who have studied the situation the future of molybdenum steels, containing 1 per cent. or under of molybdenum, is very promising and for that reason the properties of some of these steels are appended. The figures in Table 123 are kindly furnished by Dr. Sargent, Chief Metallurgist of the Crucible Steel Company. Dr. Sargent has recently presented a comprehensive discussion of the use of molybdenum in steel metallurgy at the annual meeting of the American Society for Testing Materials, 1920.

TABLE 123.—PROPERTIES OF COMPLEX MOLYBDENUM STEELS
Composition: C 0.25–0.40; Cr 0.80–1.00; Mo 0.75–1.00

Drawn at, °F.	Water quench—1600° F.					Oil quench—1700° F.				
	E. L., 1000 lbs. per sq. in.	T. S., 1000 lbs. per sq. in.	Elong- ation, per cent.	R. A., per cent.	B. H. No.	E. L., 1000 lbs. per sq. in.	T. S., 1000 lbs. per sq. in.	Elong- ation, per cent.	R. A., per cent.	B. H. No.
Not drawn	174	190	12.2	50.6	
200	170	186	12.4	52.0	360
400	166	182	12.4	53.2	360
600	209	235	11.2	44.6	440	163	178	12.4	54.8	360
800	207	226	11.8	48.0	440	159	174	12.8	56.0	340
1000	194	209	13.6	53.0	380	150	164	15.0	58.0	330
1200	163	177	18.4	60.4	300	131	143	19.2	62.6	300
1400	99	100	30.0	73.8	200	78	102	26.4	72.0	200

Material treated in form of $1\frac{1}{4}$ in. square bars and then machined to standard test bar size.

Composition: C 0.25–0.40; Cr 1.00; Va 0.15; Mo 0.75–1.00.

Oil quench—1600° F.

Drawn at	E. L., 1000 lbs. per sq. in.	T. S., 1000 lbs. per sq. in.	Elong- ation, per cent.	R. A., per cent.	B. H. No.
600°F.....	216	240	9.0	38	495
800°F.....	206	225	11.0	46	477
1000°F.....	196	210	14.2	52.4	444
1200°F.....	174	186	18.2	59.2	402
1400°F.....	90	120	27.0	65.4	241

Material treated in form of $1\frac{1}{8}$ in. round bars and then machined to standard test bar size.

The following figures were obtained by the United Alloy Steel Corporation with a chrome-nickel-molybdenum steel such as was

used for Liberty engine crank shafts. The composition was: C 0.30; Mn 0.69; Cr. 0.98; Ni 3.05; Mo 0.54. The bar was annealed at 1600–1605°F. cooled in air, treated at 1475°F. for one half hour and quenched in water and then drawn at 1150°F. for two hours and cooled in air. The figures given for this steel, taken from a publication of the Climax Molybdenum Company, are elastic limit, 130,000 lbs.; tensile strength, 142,000 lbs.; elongation on two inches, 20.5 per cent.; reduction of area, 65.0 per cent.; Brinell number, 303 and Izod impact number, 67.

We may sum up the advantages of these steels somewhat as follows: (1) These steels can be produced with exceptionally high elastic limits without sacrificing ductility and toughness. (2) The quenching and tempering ranges are particularly large. (3) When annealed the steels are soft and easily machined. (4) When in the heat treated condition, the elastic limit can be left exceptionally high without sacrificing machinability. This latter point has particular significance in the commercial production of high grade machine parts.

The principal difficulties encountered with these steels are in producing them of uniform composition without undue loss of molybdenum and in forging them for rough machining. Neither of these seems to be unsurmountable, although the shorter range of forging temperature and the more accurate control of forging temperatures imply increased losses and costs.¹ Furthermore there is too little information concerning these steels available, for example the published results deal almost exclusively with tensile or static tests and the degree to which toughness is developed can not be said to be generally known.

Summary.—We have now covered the important ternary and quaternary steels which are used for construction purposes, the ones which stand out prominently as satisfying the general requirements placed upon steels of this class. Other steels have been developed which were very promising at some time or other but which have failed to meet some of the requirements and, therefore, are not generally used at present. A new steel to compete with the nickel or chrome-nickel or chrome-vanadium steels would have to be able to withstand considerable buffeting

¹ Work done in the author's laboratory has verified a number of the points advanced here. BIERMAN and MOFFAT, Metallurgical Thesis on chrome-nickel-molybdenum steel.

by way of experimentation and testing before it would win a place among the recognized steels.

In the earlier days of the special steels, considerable was written concerning the relative merits of the different grades, as well as the special advantages of each type, in particular as compared with carbon steel. One of the first of these papers was by Le Chatelier¹ who discussed the particular advantages of special steels as construction steels. He pointed out that the purpose of the addition of the special elements was to increase the toughness; that it was quite possible to produce high tensile strength in carbon steel but that only by adding a special element was it possible to secure the combination of high tensile strength, ductility and toughness.

This increased toughness can be utilized in three different ways, according to Le Chatelier: (1) Parts can be made appreciably lighter, maintaining at the same time the same strength and toughness. This is of particular importance in the automobile industry where weight is such an important factor. The cost of production may also be reduced, due directly to the lower weight of the parts which must be handled. (2) Maintaining the same weight and toughness, the parts can be more heavily loaded, which lessens the danger of over-loading and severe straining. (3) Maintaining the same weight and strength, much greater toughness can be secured, which materially lessens the liability of failures and, therefore, of serious accidents or delays.

Guillet has also summed up the special advantages and properties of the special steels.² He points out that the objects of using special steels are (1) to increase the safety by using stronger and tougher materials; (2) to decrease the weight of the parts; and (3) to secure certain particular properties or combination of properties. In this it is sought to obtain (1) high resistance to shock; (2) high elastic limits; and (3) resistance to abrasion. Steels under the first class should have high resistance to impact when tested in the form of notched bars. The γ nickel and manganese steels satisfy this requirement as they give 40 to 50 kgm. per sq. cm. but they possess the great disadvantage of having abnormally low elastic limits. A steel of this type contains

¹ *Rev. de Metallurgie*, 1904, Vol. 1, p. 574.

² "Special Alloy Steels and their Mechanical Applications," *Engineering Magazine*, 1908, Vol. 36, p. 65.

For parts which are subject to shock he recommends (a) where a low elastic limit is not dangerous, the difficulty in working is not serious, and the price does not count, the use of high manganese or nickel steel; (b) in ordinary cases, nickel steel improved by either chromium or vanadium; and (c) where the maximum elastic limit is required but with an appreciable amount of toughness, the use of two different types of steel according to the treatment. First, for use after a simple treatment, he recommends a steel with 0.25 to 0.35 per cent. carbon and 5 to 6 per cent. nickel which when heated to red heat and allowed to cool in the air has the following properties: tensile strength 99,500 to 114,000 lbs. per sq. in., elastic limit 85,000 to 99,500 lbs. per sq. in., elongation 25 to 20 per cent., reduction of area 60 to 70 per cent., resistance to shock 25 to 35 kgm. The carbon should be under 0.4 per cent. when strength, ductility, and toughness are required, in Guillet's opinion, while manganese, chromium, tungsten and molybdenum steels are not of interest. The quaternary steels suggested are the chrome-nickel, nickel-vanadium, and chrome-vanadium steels. An example of a chrome-nickel steel for the "simple treatment" is one with carbon 0.25, nickel 5.5. and chromium 1.0, which, after annealing, has the following properties: tensile strength 99,500 lbs., elastic limit 85,000 lbs., elongation 25 per cent., reduction of area 70 per cent., and resistance to shock 35 kgm.; air hardened at 800°C. the properties are—tensile strength 121,000 lbs., elastic limit 99,500 lbs., elongation 18 per cent., reduction of area 55 per cent., and resistance to shock 25 kgm. The disadvantages of this steel are the high cost and the fact that the composition must be accurately maintained in the manufacture. Another simple treatment is that of quenching in water or in oil without tempering, which is possible with certain compositions of both chrome-nickel steel and nickel-vanadium steel.

Secondly, as the most common steels for the complex treatment (quenching in oil or water followed by tempering) he recommends the nickel steels, chrome-nickel steels, and the silicon steels, which have been considered in detail in the foregoing.

Steels which must be resistant to abrasion generally contain considerable carbon and chromium. If the parts must resist shock as well, the steels used are nickel steel, both simple and complex, silicon steels and chrome-vanadium steel. An air hardening steel of this type contains 0.40 per cent. carbon and 5.75 per cent. nickel, while a good chrome-nickel steel contains 0.35 per cent. carbon, 2.5 per cent. nickel, and 0.5 per cent. chromium, and should be quenched from 800°C. and tempered at 500°C. 0.2 per cent. vanadium is also added to this steel. These steels are used for shafts, gears, axles, spindles, etc., which must be sufficiently hard to resist wear, and still have a considerable degree of toughness.

For some parts, great hardness is the only requirement so that there are only two factors, besides cost, to consider in the choice of the steel; first, hardness, and second, ability to harden without producing flaws. Ball bearings are mentioned as an example, as they must be hard but require no toughness. The steels used generally contain 0.5 to 2 per cent. chromium, and 0.8 to 1.4 per cent. carbon. The advantages of using special steels in case hardening practice are mentioned and will be discussed more fully in Part III.¹

Longmuir has published the results of an investigation on high tension steels which was conducted in an attempt to determine the best steel for strength and endurance.² Nickel, chrome-nickel, and chrome-vanadium steels were considered. The

¹ REVILLON has also discussed the steels used in construction, *Rev. de Met.*, 1909, Vol. 5, p. 53 and *Metallurgie*, 1908, Vol. 5, p. 217, while GUILLET gave a general summary of his work in *Rev. de Met.*, 1905, Vol. 2, p. 350. GUILLET has also written a general treatise on the heat treatment of special steels in *Rev. de Met.*, 1910, Vol. 8, p. 489, in which he points out (1) that the dissolution of cementite is more difficult in special steels, and (2) that Mn, Cr, V, W, and Mo steels are sensitive to annealing while Ni and Si steels are not as greatly affected, which simplifies heat treatment after the cementation process. He also remarks that polyhedral steels are quenched in water to soften them and to make them more workable but he condemns the practice as it lowers the elastic limit. This lowers their resistance to vibrations which accounts for accidents which have occurred with these steels.

² *Journ. Iron and Steel Inst.*, 1909, No. 1, p. 382.

average requirements for commercial high tension steels, in not too large sections, are said to be—tensile strength 112,000 lbs. per sq. in., elastic limit 90,000 lbs., and an elongation on two inches of 20 per cent. He reports as the best steel the one containing about 1 per cent. chromium and 0.2 per cent. vanadium which gave results exceeding the average requirements.

That chrome-vanadium steel is the best of the three steels treated was stoutly opposed in the discussion. Examples of results obtained with chrome-nickel steel forgings were cited showing better results than those for the chrome-vanadium steels cited in the paper.

In 1909, Guillet stated that in the selection of special steels there was a tendency toward the pearlitic steels which in the order of their importance were nickel, chrome-nickel, vanadium with or without nickel and chromium, silicon and tungsten steels.¹ Examples of air hardening steels which may have a brilliant future are quoted in Table 124.

TABLE 124.—AIR HARDENING STEELS

C	Ni	Cr	Mn	Si
0.75	3.80	1.30	0.50	0.20
0.25	5.40	0.50	0.30	0.20
0.37	4.80	0.90	0.40

For gear steels he advised the use 0.4 per cent. carbon, except in silicon steel, when 0.6 per cent. carbon is required.

Revillon has considered the use of special steels for gears.² He divides the steels roughly into two classes—those containing nickel with or without chromium, and those containing no nickel. Steels may be found in either class suitable for gears but those containing no nickel, while inexpensive, are quite brittle,³ which applies in particular to the silico-manganese steels. When nickel is added, highly satisfactory steels are obtained, for either a complicated heat treatment or a simple heat treatment, according to the composition.

The use of special steels for work at elevated temperatures has been considered by Guillet⁴ who states that nickel steels

¹ *Proceedings* of the 5th Congress, International Society for Testing Materials, Copenhagen, 1909, Section I₂. Also, *Iron Age*, 1910, Vol. 84, p. 916.

² *Carn. Sch. Mem.*, Iron and Steel Inst., 1909, Vol. 1, p. 161; also *Iron Age*, 1909, Vol. 85, p. 280.

³ Chrome-vanadium steels were not considered.

⁴ *Rev. de Met.*, 1915, Vol. 11, p. 969.

with either chromium or tungsten have a tensile strength of about 30,000 lbs. per sq. in. at 800°C. Nickel steels are also very serviceable at low temperatures on account of their remarkable retention of ductility. The use of special steels for valves for internal combustion engines has been thoroughly investigated by Andrews¹ whose work will be referred to under Technical Practice.

It may be well, at this place, to point out two factors which have special significance in the commercial production of certain heat treated parts. One is that by judiciously selecting the compositions, having particular regard for the carbon, nickel and chromium, the results desired (*i.e.*, of the heat treatment) can be much more readily obtained than would be the case were no nickel and chromium present. In the case of large forgings this applies with particular force, and it would seem that the utility of using special steels in such cases is due not alone to the effect of nickel and chromium, *per se*, on the properties, but largely to their effect in improving the efficiency of the heat treatment. Secondly, it is recognized that special steels produce different relationships between the usual mechanical properties and the machinability and that, therefore, we can produce parts having increased strength, as compared to carbon steels, and still pass them successfully through the manufacturing operations. It is also known that, of two steels, the more expensive one may actually produce cheaper parts on account of the lower cost of machining it.

Duisburg has considered the use of special steels in chemical apparatus for use at high temperatures. He suggests chromium, tungsten, and molybdenum steels for this purpose and cites, as an example of an alloy which can be used, 60 per cent. chromium, 35 per cent. iron, and 2 to 3 per cent. molybdenum, which is not attacked by boiling aqua regia.

The chromium, tungsten and vanadium steels are strong at high temperatures and are very serviceable in steam turbines and vessels for chemical uses at high temperatures and high pressures.

The electrical resistance of nickel, manganese, chromium and tungsten steels as affected by variations in carbon, in the added element, and in the heat treatment, have been studied by Boudouard.² He found that Benedick's formula applied to the

¹ ANDREWS, *Engineering*, 1919, Vol. 108.

² *Compt. Rend.*, 1911, Vol. 153, p. 1475; *Rev. de Met.*, 1912, Vol. 9, p. 284.

special steels and that the resistance of tungsten steel is little affected by its heat treatment, with the reservations already made.

The thermo-electric properties of special steels, including carbon, nickel, chromium, molybdenum, manganese, aluminum, silicon, and tungsten steels in both the annealed and hardened states, have been determined by Dupuy and Portevin.¹ The curves for nickel, manganese, silicon and aluminum indicate that the metals form solid solutions, while the curves for chromium, tungsten, and molybdenum indicate that the added metal, at least after a certain composition is reached, forms a double carbide with iron and carbon.

The magnetic properties of iron, steel, and the special steels of chromium, silicon, phosphorus, and tungsten have been investigated by Gray and Ross at room temperature and at -190°C . and the results contributed in a paper read before the Faraday Society, April 23, 1912. They found in general that -190° lowers the permeability for low values of B and increases the permeability for high values of B.

COMPLEX TOOL STEELS

Although tungsten steels, containing small amounts of tungsten had been produced previously, it was Robert Mushet who, in 1858, was the first to discover the exceptional properties of tungsten steel containing higher amounts of tungsten. The steel which he introduced, and which bore his name, was really a complex alloy steel and contained $1\frac{1}{2}$ per cent. carbon, 7-8 per cent. tungsten and 1-2 per cent. manganese. This steel was noted for its great hardness, fine grain, and exceptional cutting ability, although its extreme hardness limited it to special work. Somewhat later its air hardening property was accidentally discovered from the superior cutting ability exhibited by a tool, which on being taken from a hot fire, had accidentally fallen on the floor in a position to receive the direct draft from a near-by door. After this experience the steel was heated to a golden-yellow and cooled in air. For a considerable period the Mushet tool steels controlled the market as the most efficient tool steel.

The first improvement on Mushet steel came with the substitution of chromium for manganese. This was done by a number of firms in the beginning of the nineties. A typical example

¹ *Journ. Iron and Steel Inst.*, 1915, No. 1, p. 306.

is a steel with about 1 per cent. carbon, 0.2 per cent. manganese, 2 per cent. chromium, and 8 per cent. tungsten, produced by the Midvale Steel Company in about 1894.

At about the same time, Taylor and White were conducting their extended investigation into the factors which affect efficiency and economy in plant manufacture on a large scale. One of the most important of these factors was the cutting speed of tool steel, especially on such work as the rough machining of large forgings and castings. Consequently they took up the study of tool steel and experimented on various compositions and heat treatments until finally they developed what is now known as high speed steel, or what might better be called the high speed steel treatment, for the discovery was not of a new product but of an improved method of heat treating Midvale tool steel. This important discovery of the effect of high quenching temperatures on the cutting ability of chrome-tungsten steel was made at the Bethlehem Steel Company in 1898 and first made public at the World's Exposition at Paris in 1900. At that time the altogether remarkable fact was demonstrated that a tool steel could cut so rapidly that its cutting edge actually glowed and the chips were colored a deep blue.

After this discovery that the chrome-tungsten steels possessed the valuable property of "red hardness," further investigations were pursued to obtain the most suitable compositions. It is interesting to note that while other firms have also investigated the field very thoroughly, the proportions of carbon, chromium, and tungsten in high speed steel as finally laid down by Taylor and White are still very closely adhered to. The first high speed steel exhibited contained over $1\frac{1}{2}$ per cent. carbon, 4 per cent. chromium, and 8 per cent. tungsten. By heating this steel nearly to its fusion point and quenching it in oil, its cutting ability was increased very considerably over that of the Midvale Steel as ordinarily hardened, which had given the best results up to that time. This steel, after suitable heat treatment, was regarded as a new metallurgical product and was soon being copied by tool steel makers all over the world.

One of the earliest contributions on high speed steel is that of Gledhill,¹ in which are described high speed steels as made by Armstrong, Whitworth & Company. It was the experience of this firm that carbon has the same influence in high speed steel

¹ *Journ. Iron and Steel Inst.*, 1904, No. 2, p. 127.

which it has in carbon steel, and the best steels were found to be those containing from 0.4 to 0.9 per cent. carbon. No definite limit was cited as to the correct amount of chromium although the steel generally used contained 3.5 per cent. It was not found desirable to increase the tungsten above 16 per cent. and the regular steel contained 13.5 per cent. Molybdenum was found to exert a more powerful influence than tungsten and to lower the hardening temperature. Silicon was found to harden the steel and, up to 3 per cent. to increase the cutting efficiency but, at present, this element is used only in small amounts to produce sound ingots. The methods of treating high speed steel and the advantages derived from its use were thoroughly discussed.

The following year the results of research into the microstructure and critical ranges of high speed steel, in the first attempt to explain the constitution, were contributed by Carpenter,¹ but before considering Carpenter's work it may be well to review certain preliminary work which had been done up to that time. Boehler² came to the conclusion, after a microscopic and thermal investigation of a chrome-tungsten steel, that the austenite \leftrightarrow pearlite transformation takes place at increasingly lower temperatures as the heating temperature is raised, so that the hardness of high speed steel is due to the hardening carbon and the cutting efficiency to the fact that the hardened state is converted by chromium and tungsten into the stable state.

Le Chatelier pointed out at about the same time, with his characteristic insight, that tungsten has a considerable effect in retarding the tempering of quenched steel and that the same was undoubtedly true of chromium.³ Osmond, at the same time, advanced a theory of high speed steel which is even today very useful. According to his conception high speed steels are hyper-eutectoid and contain normally an excess of carbide. By heating the steel to a high temperature the carbide dissolves and changes the composition of the γ iron solid solution, by which action the critical points are lowered. The dissolution of the carbide on heating is very sluggish and once dissolved its diffusion is very slow. This gives rise to a non-homogeneous steel which can, and often does, exhibit two heat effects on cooling. This was

¹ *Journ. Iron and Steel Inst.*, 1905, No. 1, p. 433.

² *Wolfram und Rapid Stähle*, 1903.

³ *Rev. de Metallurgie*, 1904, Vol. 1, p. 334.

verified by Carpenter who found by thermal analysis of a steel with 0.55 per cent. carbon, 3.3 per cent. chromium, and 13.5 per cent. tungsten, that raising the heating temperature has the same effect on high speed steel that it has on tungsten steel; *i.e.*, raising the heating temperature to 1000° and above, introduces a lower critical point at about 400°C. in addition to the normal critical point at about 720–740°C. Heating curves show heat effects at about 780° and 830°C. Little can be said as to the quantitative effect of tungsten on the tempering of the steel although the heating curves show no evidence of tempering below 500–600°C. It was concluded that the action of tungsten

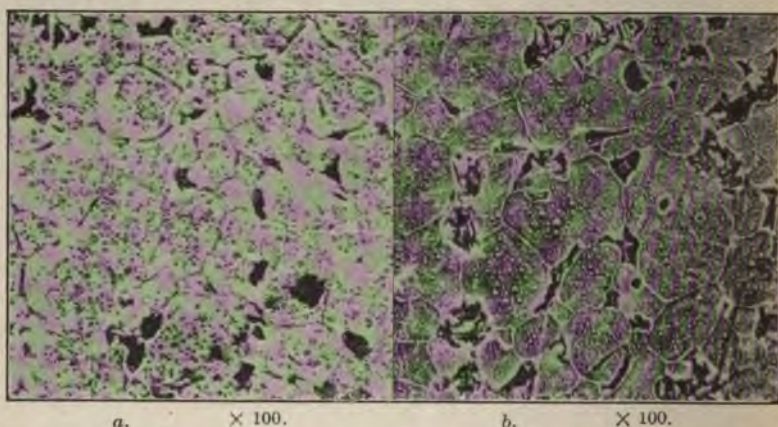


FIG. 140.—High speed tool. *a* represents structure after hardening. *b* represents structure of the cutting edge after failure.

(and molybdenum) is to prevent or hinder the tempering effect which, in the iron-carbon alloys, would result in the softening of the material. Molybdenum was again found to be more effective, weight for weight, than tungsten.

This work was continued by Carpenter who presented a second paper on "Tempering and Cutting Tests of High-Speed Steel."¹ The rate at which the temper of quenched high speed steel is drawn by reheating was very closely followed. A considerable change in the microstructure corresponding to the break-down of the usual polygonal structure of quenched high speed steel and the formation of a constituent having the appearance of troostite was noted. This break-down was gradual and com-

¹ *Journ. Iron and Steel Inst.*, 1906, No. 2, p. 377.

menced at about 500 to 550°C. and was complete at 650–700°C. This effect has also been noted by the author in an investigation of a high speed tool which had an exceptionally good cutting record. Figure 140a shows the normal structure of the heat treated tool, while Fig. 140b shows the structure at the point where the cutting edge had failed. The new product appears to be troostite. It was also noted by Carpenter that the time of etching decreased very greatly as the break-down proceeded. It was also noted, what is very important, that to secure the maximum resistance to tempering it was necessary to heat for quenching at least to a certain temperature which was found to be about 1100°C. for the usual composition. The results did not indicate that it was worth while, at least for the compositions studied, to heat above this temperature for quenching, the only effect being to increase the grain size.

One steel containing about 0.4 per cent. carbon, 3 per cent. chromium and 4 per cent. molybdenum, was found to resist tempering up to 800–900°C., or much better than steel with about 0.6 per cent. carbon, 3 per cent. chromium, and 13 per cent. tungsten. Cutting tests, however, showed the molybdenum steel to be of little value except when cutting the milder grades of steel. This shows that the relation between the cutting efficiency of a tool and the resistance to tempering is at least not simple.

A short time later, Taylor in his presidential address on "The Art of Cutting Metals,"²¹ pointed out the difference between hardness as ordinarily understood and red hardness, which he termed the

"peculiar property of chrome-tungsten steels through which it retains the cutting hardness when heated to a red heat by the friction of the turnings passing over the tool." Taylor remarked further, regarding red hardness, that "after being heated close to the melting point, tools were immediately buried in lime, in powdered charcoal, and in a mixture of lime and powdered charcoal; then they were cooled extremely slowly, hours being required for them to get below a red heat. And we wish strongly to state the fact that tools cooled even as slowly as this, while they were at once once quite soft and could be filed readily, nevertheless retained the property of 'red hardness' in as high a degree as the very best tool."

²¹ *Trans. Amer. Soc. Mech. Engineers*, 1907, p. 4.

Taylor pointed out that the loss of red hardness takes place over the temperatures from 650°C. to 730°C. and that this critical interval is indicated neither by Professor Carpenter's heating curves nor by his observations of the microstructure. Taylor stated in particular that there is no relation between the quality of the tool and its microstructure. Such a conclusion, at that time, is certainly to be regarded as premature, especially as it was not substantiated by satisfactory evidence. The effect of vanadium of increasing the hardness and endurance of high speed steel was also noted.

The discussion of this paper was immediately taken up by Professor Carpenter.¹ In his discussion, Professor Carpenter quotes from Mr. Taylor's address as follows:

"Our original investigations showed that red hardness was seriously impaired by heating tools above 650°C. and that the quality of red hardness was entirely removed by heating them up to 730°C. Now it will be noted that neither in the heating nor cooling curves shown by Professor Carpenter any critical point is shown at these temperatures which are the critical temperatures so far as we know for high speed steels and therefore the critical temperatures affecting red hardness."

Professor Carpenter points out that, contrary to the deductions of Taylor, heating curves of high speed steel show a change in slope beginning at about 620°C. and continuing up to about 735°C. This is commonly referred to as an Ar point on a heating curve which is the phenomenon first observed by Osmond in 1885.² Professor Carpenter then advanced the theory that high speed steel, by virtue of the chromium and tungsten present, may be retained in their austenitic state by rapid cooling from 1200°C.³ The combined chromium and tungsten present prevent the drawing of the temper up to 500–550°C., while at 600°C. austenite is said to change to martensite. Thus it is explained that high speed steel differs radically from quenched carbon steel.

¹ *Engineering*, 1907, Vol. 83, p. 569.

² *Journ. Iron and Steel Inst.*, 1890, No. 1, p. 38. See Plate V. See also, OSMOND and WERTH, *Annal. des Mines* 1885, Vol. 8, p. 5. OSMOND showed that the liberation of the heat of hardening of quenched carbon steel commences at about 200°C., reaches a max. at about 350°C. and appears to cease at just above 500°C.

³ The assumption of the austenitic state of treated high speed steel is used to explain the fact advanced by TAYLOR that tools of high speed steel may be readily filed.

According to this explanation, the hardness of ordinary quenched carbon steel is conferred upon high speed steel by heating to a dull red heat, the temperature at which the steel is known to have the best cutting properties, "and no distinction seems necessary other than that the hardness is manifested at different temperatures. The hardness itself is the same in the two cases."

Professor Carpenter remarked immediately, however, that the martensitic structure did not always form under these conditions and that the explanation should not be assumed to be general.

The important rôle of chromium in high speed steel, especially in conferring the property of red hardness, was also discussed. Taylor pointed out that "a tool without chromium, or with very low chromium, even though there is a proper percentage of tungsten present, does not produce a high speed steel although the manganese may be very low or very high." Professor Carpenter remarked that the tendency of chromium as an accelerator rather than as a retarder of the reactions, tends to convert the austenite of quenched high speed steel into martensite, a conversion which does not take place in the absence of chromium.¹

At about this time Guillet contributed an important paper on chrome-tungsten quaternary steels.² This investigation was carried out particularly to determine the most suitable compositions for high speed steel. In general, the chrome-tungsten steels have the following microstructures, depending upon the amounts of carbon, chromium, and tungsten: (1) pearlite, (2) martensite, (3) martensite + carbide, (4) carbide in γ iron, (5) carbide in troostite. In the investigation of the high speed steel composition, it was found that (1) by increasing the carbon the ground mass changes from martensite to troostite and troostosorbite; (2) increasing the tungsten has no influence except to increase the amount of carbide present, which also holds for (3) chromium.

¹ According to EDWARDS (*Journ. Iron and Steel Inst.*, 1908, No. 2, p. 104), the function of tungsten is to form a carbide at about 1200°C. which combines with chromium to form a double carbide. This carbide remains in solution on cooling but is decomposed on reheating to 670°–830°C. A somewhat similar theory was advanced by SPÜLLER (*Chem. Zeits.*, 1903, p. 165).

² *Journ. Iron and Steel Inst.*, 1906, No. 2, p. 114.

The structure of high speed steel was found to be carbide + sorbite, in which case the carbon, in order to prevent the formation of martensite, must be above 0.5 per cent. Such a structure is shown in Fig. 141. Mechanical tests made on these steels showed the following: (1) The pearlitic steels have high tensile strengths and elastic limits and low elongations but the resistance to shock is greater than in ordinary steels. (2) The martensitic steels are very strong and hard but lack ductility and toughness. (3) The steels with martensite + carbide are strong with medium



× 400.

FIG. 141.—Structure of annealed high speed steel.

elongation, and are brittle and hard. (4) The steels with carbide + sorbite have the same properties as given under (3). The properties vary but little with the composition except that the elastic limit increases slowly with carbon and chromium and is low for high tungsten. (5) Steels with carbide + γ iron have low tensile strengths and elastic limits, are brittle and have little resistance to shock. These steels, even though having elongations from 10 to 15 per cent., have low resistance to shock when the carbide is present.

Quenching high speed steels in water from 1250°C. after five minutes, produced martensite + carbide, the carbide of which increases with carbon, chromium and tungsten. Increasing the time at 1250°C. lowers the amount of carbide present in all the steels examined. One-half an hour was sufficient to destroy all

the carbide on quenching at 1200°C.¹ The time necessary to do this increased with carbon, chromium and tungsten and was also greater at lower temperatures. The results obtained by quenching from 850°C. were also contributed but will not be discussed here.

It was found with a steel containing 0.53 per cent. carbon, 3.2 per cent. chromium and 14 per cent. tungsten that the maximum hardness on quenching in water from 1200°C. was obtained by heating for 10 minutes, while the maximum at 900°C. was obtained after heating for 15 min. The rate of cooling had only a slight effect on the hardness but the more energetic cooling, by retaining γ iron, produced softer steels. Microscopic examination showed that the maximum hardness came with the disappearance of the carbide constituent. Forging tests, while not conclusive, indicated the proper forging temperature to be from 950°C. to 800°C.

The relations between carbon, chromium, and tungsten to produce high speed steel were found to be as follows: (1) The sum of the carbon, chromium and tungsten contents must be high so that neither pearlite nor martensite forms on slow cooling; (2) the more there is of one of these constituents, the less is needed of the third element to give carbide and troostite; (3) chromium must not be too high because, if it is, γ iron forms. The tungsten can vary considerably but its correct amount depends upon the carbon content. The end sought (for the composition cited above, it should be pointed out) on quenching is to avoid γ iron, and to produce fine grained martensite containing no carbide, so that a properly treated high speed steel ready for cutting should not show any well defined constituent. To obtain this, heating at 1200°C. for ten minutes is sufficient. Case hardening high speed steel increases the amount of carbide constituent and converts the martensitic structure into troostite.

The work so far had not satisfactorily explained the metallography and cutting properties of high speed steel. It had not shown, for example, the exact relations between the quenching temperature, the temperature at which quenched high speed steel is known to lose its property of red hardness, and the microstructure; neither had Taylor's "simple index" to the property of red hardness been found.

¹ The compositions investigated in this series contained about 13 per cent. tungsten.

In an attempt to elucidate certain of these questions, an investigation into the effect of chromium and tungsten upon the hardening and tempering of high speed steel was conducted by Edwards and Kikkawa.¹ The steels which were used contained about 0.6–0.7 per cent. carbon, one series with constant chromium and increasing tungsten contents and another series with constant tungsten and increasing chromium contents. The steels were quenched from 1350°C. after ten minutes, by cooling in an air blast. The structure aimed at in the hardened state was the austenitic structure. The samples were then examined under the microscope and tested for hardness and then heated for one hour at successively increasing temperatures up to 1000°C. The Brinell hardness was found to increase from 627 for the hardened specimen to 700 for the same specimen reheated for two hours at 590°C. (composition: carbon 0.64, chromium 6.24, tungsten 17.69). Further increase in reheating temperature caused a considerable drop in the Brinell hardness. Reheating for a period of five minutes raised the maximum hardness to 732 which was produced at a temperature of 614°C.²

According to the authors, the steel changed from the polygonal structure to the martensitic structure on being reheated. Above the temperature at which the maximum secondary hardness is produced, the martensitic structure is said to disappear, the interval extending up to 700 to 750°C. It was stated that chromium unquestionably imparts the property of self-hardening to these steels. Its functions are stated as follows: "(a) In conjunction with carbon it is the cause of the great hardness of high speed steel; and (b) it produces a marked lowering in the temperature at which hardening can be effected." Tungsten is said to raise the temperature at which tempering (loss of red hardness) begins, and in the presence of chromium, to increase the secondary hardness. Chromium was also found to increase the solubility of tungsten in steel; thus, with 6 per cent. chromium, 19 per cent. tungsten can be held in solution at 1350°C. To get the maximum results from modern high speed steel, it is necessary to heat at least to this temperature. When heated above this temperature, partial liquification takes place which, on quenching, gives rise to a hard constituent outlining the borders of the poly-

¹ *Journ. Iron and Steel Inst.*, 1915, No. 2, p. 6.

² This same effect had already been contributed by DENIS.

gons.¹ Specific gravity determinations brought out that an increase in specific volume accompanies the increase in secondary hardness.

Chromium, as a self-hardening agent, was further investigated by Edwards in conjunction with Greenwood and Kikkawa.² In the discussion of the paper, Professor Carpenter remarked on the difference of opinion which had arisen relative to chromium as a self-hardening agent, and drew the interesting conclusion that while the views held by the two groups on this point were opposite to each other, inasmuch as the information was inadequate, neither side was either entirely right or entirely wrong. Thus Edwards, Greenwood and Kikkawa found that the property of self-hardening is governed by the rate of cooling and that there is a critical cooling velocity above which chromium imparts self-hardening and below which no effect is produced. The critical cooling velocities were found to be much lower as the initial or heating temperature was raised. Whether or not the steel were self-hardened could be regularly determined by the microscope which showed the characteristic martensitic structure for the hard steel. The maximum hardness was obtained when the rate of cooling was such that the thermal transformation was entirely suppressed; steels of this nature possessed simple martensitic structures.

An interesting explanation of the effect of increasing the heating temperature on the self-hardening property of chromium steel was advanced. The carbide Cr_6C_4 is supposed to go into solution first, and then to dissociate into Cr_3C_2 as the temperature is raised. On cooling the association takes place very slowly leaving a much greater number of molecules in solution (Cr_3C_2 as compared to Cr_6C_4) and increasing the osmotic pressure so that the transformation point is more readily suppressed.

Critical Point Curves of High Speed Steel.—Andrew and Green have shown that high speed steel normally has a small heat effect at about 775°C . and a larger one at 850°C . in terms of the maxima on heating. The heat effects on cooling depend upon the maximum heating temperature (T_{max}). If heating is

¹ From this paper it would be assumed that such steels would give unsatisfactory results, which is not the case in actual practice as some of the best cutting records have been obtained with tools showing this microstructure. See Fig. 138.

² *Journ. Iron and Steel Inst.*, 1916, No. 1, p. 114.

stopped at about 900°C., one heat effect occurs at about 750°C., while if heating is carried above 1000°C. a lower effect at about 400° displaces the upper effect. By carrying the heating up to 1300°C. the temperature of the lower effect is gradually lowered to about 380°. As $T_{\text{max.}}$ is raised, the amount of heat given off and the Brinell hardness are increased. In general we may say that if only the upper heat effect occurs, the steel is in the soft or annealed condition, while if only the lower effect occurs, the steel is in a semi-hard or hard condition. A question arises here as to the nature of the lower effect and why it is not observed on heating curves, or in general, why it is that a transformation, with which such a large heat effect is associated, does not interfere with the cutting efficiency of tools at appreciably higher temperatures. Even a cooling from 1300 to 250°C. in 96½ min. leaves the steel appreciably hard (B. H. = 532) and, presumably, the steel would still show high speed cutting properties.¹ This shows that there is some important change between 1000° and 1300°C. and that the complete development of this action is essential to the proper hardening of high speed steel.

The Hardness of High Speed Steel.—Considerable confusion has arisen as to what is meant when the “hardness” of high speed steel is mentioned. It is now well known, however, that the hardness of a piece of steel as quenched is not an index to the cutting efficiency of the tool. A review of the literature, such as has just been made in the preceding pages, indicates in no way that there was any confusion in the minds of the experimenters on this point. Determinations of the hardness have been made but it has always been the ability with which the quenched steel retains its hardness or the extent to which it acquires secondary hardness, which has been paramount. In fact, it was early pointed out by Taylor, in 1905, that there existed a vast difference between hardness at room temperature, and hardness and ability to retain hardness at a dull red heat. It was pointed out by Edwards and Kikkawa² that the improvement in cutting efficiency by heating to near the melting point

¹ ANDREW and GREEN, *Journ. Iron and Steel Inst.*, 1919, No. 1, p. 305. This work on critical points agrees with that of Yatsevitch, (*Rev. de Met.* 1918, Vol. 15, p. 65) and of the writer. (Mr. C. Q. Swenson, Research Assistant.) The lower heat effect on heating was found to be a magnetic transformation, and to occur at the same temperature on cooling if the upper heat effect were not passed through.

² *Ibid.*, page 20.

"is certainly not due to an increase in the hardness of the steel, because whatever differences are observed in this connection it is invariably found that a greater hardness is produced by air quenching from the lower temperatures down to about 1000°C."

The evidence is abundant that raising the quenching temperature above 1000°C. has but little effect on the actual hardness. It was even pointed out by Taylor that a variation in the carbon content from 0.3 per cent. to over 1 per cent. has no considerable effect on the cutting efficiency of the tool.

In spite of the repeated warnings on this point and the exceptional clarity with which it has been pointed out both in private and in public, there still seems to be some misapprehension that the Brinell test might be substituted for lathe tests for judging high speed steel. Arnold, in 1916, presented a paper for the purpose of showing that there exists no direct relationship between Brinell or scleroscope hardness and cutting efficiency. That it was felt that the point was conclusively proven can be told from the discussions which were all in agreement with Prof. Arnold.

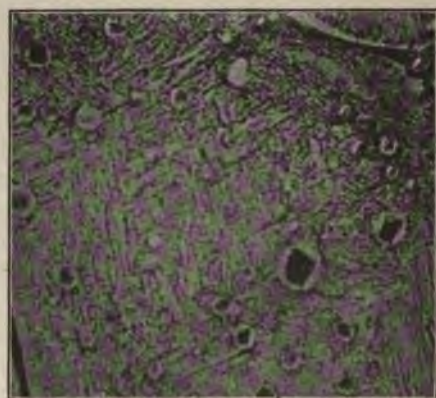
The increase in hardness due to reheating properly quenched high speed steel has already been noted. An insufficient hardening temperature lowers the secondary hardness developed and also the hardness at which the minimum in hardness is produced. (Andrew and Green.) This variation in hardness is eliminated by tempering at the temperature of the maximum.

For the sake of reference, the following table is added, which gives the author's determinations of the hardness of several grades of high speed steel in the annealed and oil quenched conditions.

TABLE 125.—HARDNESS OF HIGH SPEED STEEL

Composition								Brinell	Sclero- scope
C	Mn	Si	Cr	W	V	Co			
.61	.26	.30	3.98	11.80	1.40	Annealed	223	37
							Oil quenched	630	90-95
.69	.22	.30	4.12	12.79	1.61	Annealed	240	41
							Oil quenched	650	90-95
.76	.22	.24	4.10	13.47	1.35	Annealed	260	42
							Oil quenched	650	92-94
.70	.22	.30	2.46	20.68	1.00	5.65	Annealed	255	43
							Oil quenched	630	92-96

An interesting point, at least theoretically, in connection with the hardness of high speed steel is the nature of the constituent which forms on quenching. In the literature, the constituent is at times assumed to be austenite, and at times to be martensite, with no definite reasons for either. The writer, while engaged in a research on high speed steel became interested in the point and examined a number of bars quenched in oil as well as several tools known to have good cutting records. It was found that by carrying the etching far enough, a definite martensitic structure was brought out. Steels which were quenched from lower temperatures, and which were therefore



× 800.

Fig. 142.—Martensitic structure in properly quenched high speed steel.

quite fine grained (tools with poor cutting records showed similar structures), could not be classified either way. It seemed quite evident that the structure of properly hardened high speed steel is martensite, with or without carbide, as is shown in Fig. 142. On this basis it is difficult to explain the "secondary hardness" as determined by Edwards and Kikkawa.

Annealing High Speed Steel.—The work of Andrew and Green gives us a safe guide to the correct treatment for annealing high speed steel. This treatment would be one which heats the steel to such a temperature that the upper transformation at $740^{\circ}\text{C}.$ takes place on cooling inasmuch as it is this transformation which softens high speed steel. Andrew and Green recommend heating to 870 to $950^{\circ}\text{C}.$ and cooling slowly. A one inch square bar of steel containing 0.60 per cent. carbon, 0.09 per cent. manganese,

0.20 per cent. silicon, 14 per cent. tungsten, 4 per cent. chromium and 0.5 per cent. vanadium heated thirty minutes at 900°C. and cooled slowly in the furnace gave a Brinell hardness of 243°. Air cooling from 740°C. can be used to expedite the treatment. The temperature used in works practice was said to be 800°C. and that the treatment at this temperature is long (three days) and relatively expensive.

The Development of High Speed Steel.—Ever since the high speed steels were put on the market, metallurgists have continually attempted to improve the compositions, to produce steels with even more durable red hardness. It would be beyond the scope of the present treatise to attempt to describe this development in full, but some of the more important steps can be given.

The development of tool steel up to 1906 has been given by Taylor and is here reproduced in Table 126.

TABLE 126.—TOOL STEEL COMPOSITIONS UP TO 1906

Steel	Composition						Cutting speed, ft. per min.
	C	Cr	W	V	Mn	Si	
Jessop's carbon steel.....	1.047	0.207	0.189	0.206	16
Mushet's air-hardening . . .	2.150	0.398	5.441	1.578	1.044	26
Midvale steel. . .	1.143	1.830	7.723	0.180	0.246	
Original Taylor-White.....	1.850	3.800	8.000	0.300	0.150	58-61
High-speed steel, 1906.....	0.670	5.47	18.910	0.29	0.110	0.043	99

Cutting data are for medium-carbon forging steel.

Jessop's steel is given as typical of the best carbon steels. Mushet's steel is typical of the air-hardening steels with large amounts of tungsten, manganese and silicon. The Midvale steel, the precursor of high speed steel, was the first rival of Mushet's steel, and was likewise an air-hardening steel. Its cutting speed was found to be somewhat greater than that of Mushet's steel. The cutting speed of this steel after the high speed treatment (the original Taylor-White steel) is seen to be over twice as great as that of Mushet's steel. Further investigations resulted in increasing the tungsten to

18 per cent. and the chromium to 6 per cent. and decreasing the carbon (to avoid brittleness) to 0.6 per cent., as the cutting efficiency was not found to suffer thereby. Vanadium, which was at that time being introduced as a valuable addition to steel, was found to improve the steel and a small amount was added as a cleansing agent. The next notable advance was the increase in the amount of vanadium to 1-2 per cent., an example of which is the "Novo Superior" produced by Jones and Colver, Sheffield. This steel was first announced by Professor Arnold in a lecture held in Sheffield in January, 1909 but without naming the steel or the maker. It was given out that this "new steel" was superior to the other steels by several hundred per cent. and that it was for water hardening. The consternation in the ranks of the tool steel makers caused by this remarkable pronouncement of Professor Arnold is now a matter of history. It is sufficient to say that the steel, when it came out, was found to be but little different from other high grade steels and that its record did not at all warrant the prophesies made for it. Since then vanadium in small amounts has proved to be a very valuable addition to high speed steel. A 13 per cent. tungsten steel with 1 per cent. vanadium has about the same cutting efficiency as one with 18 per cent. tungsten with no vanadium. 2 per cent. vanadium improves the cutting efficiency still more but also increases the brittleness, and therefore the necessity for using extreme care in working and using the steel.

Vanadium is also added to 18 per cent. tungsten steel, as is shown by the following analysis of "Maximum Special" of the Poldihütte, Vienna, recognized as one of the best high speed steels: carbon 0.88 per cent., silicon 0.28 per cent., manganese 0.07 per cent. phosphorus 0.018 per cent., sulphur 0.036 per cent., copper 0.07 per cent., nickel 0.06 per cent., chromium 5.09 per cent., tungsten 18.10 per cent., vanadium 1.16 per cent., molybdenum 0.6 per cent. The addition of more than 1.25 per cent. vanadium is seldom economical on account of the increased cost.¹

The next notable step in the development of high speed steel was the introduction of about 5 per cent. cobalt. An elaborate series of lathe tests was conducted at the Royal Technical School, Charlottenburg-Berlin, from which, as reported,² the cobalt steels have a much greater durability than the usual types with-

¹ EDWARDS, *Iron Age*, 1912, Vol. 89, p. 957.

² *Stahl u. Eisen*, 1913, Vol. 33, p. 929.

out cobalt. Cobalt steel was said to possess the added advantage of a much more uniform performance, *i.e.*, excellent cutting ability whether working on mild steel, special steels or on cast iron. The composition of one of the best cobalt steels was found to be carbon 0.76 per cent., silicon 0.28 per cent., manganese 0.10 per cent., phosphorus 0.010 per cent., sulphur 0.032 per cent., copper 0.06 per cent., nickel trace, cobalt 5.03 per cent., chromium 4.38 per cent., tungsten 16.40 per cent., vanadium 0.62 per cent., molybdenum 0.3 per cent. The results, as soon as published, were protested by German and Austrian tool steel makers and to such an extent that considerable doubt was thrown upon them. At least the very great superiority exhibited by the cobalt steels in the test was considerably discounted, but it is interesting to note that firms at the present day advertise cobalt steels as among their very best steels. Cutting tests extending over a period of years show that the addition of 5 per cent. cobalt is undoubtedly a great advantage for certain heavy roughing cuts.

Of recent date uranium high speed steels have come on the market, advertised as being very high grade, but it is still too early to state definitely that they are superior to other high speed steel compositions. The author knows of impartial tests in which uranium steel, while good, was no better than other good steels and did not succeed in winning first place.¹

There is now no mystery regarding the compositions of high speed steel and the possibilities of each standard composition are fairly well known. Of greater technical interest (and importance) are the production, forging, and heat treatment of the steel and the care and skill employed therein. It is particularly important to eliminate the dendritic or ingot structure and to break up and disseminate the "carbide" uniformly throughout the bar of steel. These are points which will receive further consideration in Part III. We may summarize the steel compositions as follows. Manganese and silicon are used for securing sound steel, and for that purpose alone; they will run between 0.15 and 0.30 per cent. Sulphur and phosphorus are required to be low, under 0.030 per cent. Of the other elements, carbon and chromium are well standardized at about 0.6 per cent. and 4 per cent. respectively, allowing for minor variations. The tungsten is usually held within 13 per cent. and 18 per cent.

¹ See JOHNSON, Influence of Uranium in Tool Steel, *Journ. Amer. Chem. Soc.*, 1916.

The higher amounts of tungsten give greater cutting speeds but they also increase the brittleness, so that the tungsten is varied with the kind of work to be done. Vanadium in amounts up to about 1.25 per cent. is added to either the low or high tungsten steels to increase the cutting efficiency; 1.0 per cent. vanadium added to the low tungsten steel gives an efficiency about equal to the high tungsten with no vanadium. The addition of vanadium made it possible to quench high speed steel in water without danger of cracking. Vanadium also increases the brittleness. Cobalt is added in special cases still further to increase the cutting efficiency although the brittleness is again increased so that the field of usefulness is limited to steady continuous work under a heavy load.

Although molybdenum has not been considered here in high speed steel compositions, as an element it promises very interesting possibilities. It is much more efficient than tungsten and the steel can be successfully hardened at a lower temperature. Molybdenum steels have given some remarkable cutting records but their behavior is, on the whole, very erratic. This latter combined with other deficiencies of molybdenum have limited its use in tool steel manufacture. The well known quality of the exceptional molybdenum high speed steels which have been made has led investigators to seek a "stabilizer" for molybdenum, an element which would give the steels uniformly high cutting efficiencies. Just recently we have had a second pronouncement from Prof. Arnold to the effect that vanadium was such a stabilizer and it was widely heralded that a molybdenum steel had been discovered which was superior to the tungsten compositions. Tool steel makers again demonstrated that Arnold's composition had long since been tried out and found wanting when put into commercial production. Almost simultaneously it was announced by Sheffield steel makers that cobalt was a stabilizer of molybdenum which could be used in commercial production. If this is borne out by plant experience we can add the Co-Mo steels to other standard compositions as a successful high speed steel.

Considerable interest is being shown in steels and alloys which can be cast into bars and be ground and used for tools without forging. These are complex alloys and have not been found to compare favorably with high speed steel of the standard makes. In this group may be mentioned Stellite, an alloy of

cobalt and chromium with some tungsten, although Stellite has, as the single exception, demonstrated its exceptionally great cutting ability, which exceeds that of any high speed steel for heavy but smooth cuts.¹

Tests of High Speed Steel.—The only reliable method so far developed for testing high speed steel is that of subjecting the steel, ground to standard size and shape, to a competitive lathe test (using up to six samples for a test) with a high speed steel of known cutting ability. The lathes used may be any standard lathe, of sufficiently large size and in good running condition, but special lathes are constructed at times for this purpose.² The block of steel cut is also standard and of uniform quality as far as it is possible to secure such. This work has been largely confined to the shops where the steels are made and there has not been much published on cutting tests. Other tests are competitive tests carried out by purchasers to determine suitable grades prior to letting contracts for supplies. The results of these tests are private. Perhaps the best criterion to use in such tests is the duration of the test up to the moment of failure, assuming standard conditions of cutting speed and dimensions of the cut.

A special machine to test the cutting properties of steel has been devised by Herbert. With this machine it was possible to obtain the relationship (1) between "life" and cutting speed, and (2) between "duty" (= product of metal removed and cutting speed) and cutting speed. Curves plotted for (1) showed early maxima for carbon tool steel and higher and later maxima for high speed steels. It is interesting to note that, at low cutting speeds, carbon steels cut longer than high speed steels. The cutting speed indicating maximum "duty" is higher than the one indicating maximum "life." Double maxima were noted on certain of the curves which have been exceedingly difficult to explain satisfactorily.³ In a later paper, Herbert discussed the

¹ An application of this method to the manufacture of formed tools has been described by J. E. JOHNSON, JR., *Bull. Amer. Inst., Min. Engr., Feb., 1919*.

² See the article of Prof. SCHLESINGER cited above for the description of such a lathe.

³ *Journ. Iron and Steel Inst., 1910, No. 1, p. 206; Eng. News, 1909, Vol. 62, p. 299; Engineering, 1909, Vol. 89, p. 691.*

effect of heat and cooling liquids on the cutting efficiencies of tools.¹

Two very comprehensive treatises on the properties and cutting efficiencies (Herbert test) of carbon, special and high speed tool steels, contributed by Denis give many particulars of the properties as affected by quenching temperatures and media, drawing temperatures and compositions.²

¹ *Journ. Iron and Steel Inst.*, 1912, No. 1, p. 358.

² DENIS, *Rev. de Metallurgie*, 1914, Vol. 11, p. 4 and p. 569.

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